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Physics. — *"The Magneto-Thermic Effect according to Thermo-dynamics"*. (Supplement N°. 47 to the Communications from the Physical Laboratory at Leiden). By Prof. J. P. KUENEN †.

(Communicated at the meeting of December 30, 1922).

In experiments with ferro-magnetic substances WEISS and PICCARD [1]) found that the heat-effect which accompanies a magnetic change, assumes a relatively large value in the neighbourhood of the Curie-point. According to them this phenomenon, just as the discontinuity in the specific heat at the Curie-point [2]), is a consequence of the "molecular field", which plays a prominent rôle in WEISS' theory of ferro-magnetism.

It is natural to apply equations to this phenomenon which ensue from the second law of the theory of heat. The question suggests itself whether this is allowed, as non-reversible changes occur in ferro-magnetism. Every condition — leaving disturbances out of account — is indeed a condition of stable equilibrium, but in general the substance cannot pass through a definite series in both directions. This difficulty may be obviated by considering only those conditions that arise under the influence of strong mechanic or electric vibrations: these neutralize hysteresis, and with it also remanent magnetism, and the conditions then become reversible. The results obtained by the aid of thermodynamics, will in main lines most likely also hold for the phenomena occurring under normal circumstances: above the Curie-point they are, of course, strictly valid.

The external work of a magnetized system being represented by $- H \, d\sigma$, where H and σ denote resp. the magnetic force and the magnetisation, the chief equation of thermodynamics is:

$$d\varepsilon = T \, d\eta + H \, d\sigma \quad \cdots \cdots \cdots \quad (1)$$

As it is most convenient if H is an independent variable, we write:

$$d(\varepsilon - H\sigma) = T \, d\eta - \sigma \, dH \quad \cdots \cdots \quad (2)$$

from which follows:

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[1]) P. WEISS et A. PICCARD, J. de Phys. (5) 7, p. 103, 1917.
[2]) P. WEISS, A. PICCARD et A. CABRERA, Arch. de Genève 1917; J. de Phys. (5) 7, p. 87, 1917.

$$\frac{\partial T}{\partial H_\eta} = -\frac{\partial \sigma}{\partial \eta_H} = -\frac{T}{c_H}\frac{\partial \sigma}{\partial T_H} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Here c_H is the specific heat for constant field. This equation shows that the thermic effect in question is greatly dependent on $\frac{\partial \sigma}{\partial T_H}$, hence becomes abnormally high in the neigbourhood of the Curie-point, and this is what we intended to prove.

$\frac{\partial \sigma}{\partial T}$ being < 0, the temperature increases during the magnetisation, and reversely. According to the above-mentioned experiments c would suddenly assume a lower value at the passing of the Curie-point in upward direction, but this does not affect the conclusion drawn. The relation found is independent of WEISS' hypotheses, and sets forth the inter-relation between heat-effect and disappearance of ferro-magnetism more clearly than the equations given by WEISS and PICCARD.

When, with WEISS and PICCARD, σ is taken as independent variable, the following is found from (1):

$$\frac{\partial T}{\partial \sigma_\eta} = \frac{\partial H}{\partial \eta_\sigma} = \frac{T}{c_\sigma}\frac{\partial H}{\partial T_\sigma} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Above the Curie-point $\frac{\sigma}{H}(T-\theta) = C$, where θ and C are constants, so that $\frac{\partial H}{\partial T_\sigma} = \frac{\sigma}{C}$. On substitution of this in (4) an equation is obtained which also occurs in the cited paper, but which is strictly proved here without having recourse to WEISS' special theory.

It will be vainly tried to estimate the said change of the specific heat at the Curie-point purely thermodynamically. Thermodynamics gives, indeed, the change of c_H with the value of H (resp. of c_σ with σ), and the difference between c_H and c_σ, but not the dependence on the temperature in question. To find this a molecular theory like that of WEISS, is indispensable. From this an expression for the internal energy ε will have to be derived, and also for the c's, because $c_\sigma = \frac{\partial \varepsilon}{\partial T_\sigma}$ and $c_H = \frac{\partial \varepsilon}{\partial T_H} = H\frac{\partial \sigma}{\partial T_H}$.

In connection with the preceding paper I may be allowed to add a few remarks.

The late Professor KUENEN had the intention to make a communication on the subject mentioned in the title at the Meeting of the

Royal Academy of Sept. 30 1922; a few days, however, before the meeting death took him away. Among the papers found after his death was the manuscript of the above communication, ready for the press, and a few detached sheets, on which the author tried to ascertain what follows from the equations:

$$c_H = c_\sigma + T \frac{\left(\frac{\partial \sigma}{\partial T}\right)_H^2}{\left(\frac{\partial \sigma}{\partial H}\right)_T} \quad \cdots \quad \cdots \quad (A)$$

$$\frac{c_H}{c_\sigma} = \frac{\left(\frac{\partial H}{\partial \sigma}\right)_\eta}{\left(\frac{\partial H}{\partial \sigma}\right)_T} \quad \cdots \quad \cdots \quad (B)$$

$$\left(\frac{\partial c_H}{\partial T}\right)_T = T\left(\frac{\partial^2 \sigma}{\partial T^2}\right)_H \cdot \quad \cdots \quad \cdots \quad (C)$$

$$\left[\frac{\partial}{\partial T}\left(\frac{c_H}{T}\right)\right]_H = \left(\frac{\partial^2 \eta}{\partial \sigma^2}\right)_H \left(\frac{\partial \sigma}{\partial T}\right)_H^2 + \left(\frac{\partial \eta}{\partial \sigma}\right)_H \left(\frac{\partial^2 \sigma}{\partial T^2}\right) =$$

$$= \left(\frac{\partial^2 \eta}{\partial \sigma^2}\right)_H \left(\frac{\partial \sigma}{\partial T}\right)_H^2 + \frac{c_H}{T} \frac{\left(\frac{\partial^2 \sigma}{\partial T^2}\right)_H}{\left(\frac{\partial \sigma}{\partial T}\right)_H} \quad \left.\right\} \quad (D)$$

which can be derived in a purely thermodynamic way, if they are combined with the empirical data on the course of $\sigma = \varphi\,(T, H)$ in the neighbourhood of the Curie-point, or with the equation:

$$\varepsilon = -\frac{n\sigma^2}{2} + f(T) \quad \cdots \quad \cdots \quad (E)$$

which is the direct consequence of the formula for the molecular field H_m used by Prof. WEISS:

$$H_m = -\left(\frac{\partial \varepsilon}{\partial \sigma}\right)_T = n\sigma \quad \cdots \quad \cdots \quad (F)$$

It seems to have been his intention to throw light on the question what suppositions are *necessary* to derive the change of the specific heat of ferro-magnetic bodies at the Curie-point.

P. E.

Chemistry. — "*Determination of the Vapour Pressure of Metallic Arsenic*". By Shinkichi Horiba. (Communicated by Prof. P. Zeeman).

Arsenic is one of the most interesting elements, which should be studied from the view-point of the theory of allotropy. It is a well known fact that arsenic can exist in three kinds of modification, i. e. gray, black, and yellow; the gray modification is quite stable in a wide range of temperature, while the others are rather metastable. Although many investigations have been carried out about this important element, yet it has never been tried to define the exact lines of demarcation between these three modifications. Recently some observations of its melting point have been reported by Goubeau[1]), Heike[2]), Rassow[3]), and some measurements of the vapour pressure of its solid phase by Heike, but in the case of the latter, an indirect method was used, so that the results were not very accurate. The vapour pressure of the liquid phase of this element has never been determined. On the suggestion of Professor Smits, the author has undertaken the measurements of the vapour pressure of this element in the laboratory of the University of Amsterdam; the object of the present study is, of course, to investigate the whole system of this element, but the author is not yet in the position to complete this study, owing to the difficulties of the technics of the measurements. The present communication will only represent the results of the measurements of the vapour pressure of the gray modification and give some thermal data which can be calculated from these vapour pressure data.

The Method of Investigation.

The same method of investigation, used by Prof. Smits and Bokhorst[4]) for the study of phosphorus, was applied; a small modification, which was made in the present investigation, was that a quartz indicator of pressure was used instead of the hard glass, in view

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[1]) Compt. rend., **152**, 1767, (1911).

[2]) Z. anorg. chem., **117**, 147 (1921): the literature of the melting point was given in this paper.

[3]) Z. anorg. chem., **114**, 131 (1920).

[4]) Z. physik. chem., **91**, 249 (1916).

of the high melting point of arsenic. Owing to the technical difficulties of making such an indicator, its sensibility was somewhat inferior to that of the indicator made of glass, still some of the indicators which were used, could keep their sensibilities within one centimeter of mercury, being sufficient for the present purpose.

The Material.

MERCK's metallic arsenic was used after several purifications. At first the finely powdered sample was subjected to repeated sublimation in a vacuum by the aid of a large Heraeus electric furnace, the temperature of the furnace was maintained at a little over 500° C. in the first sublimation and at nearly 600° C. in the final one. The gray modification thus prepared was again very finely powdered, and was extracted by carbon disulphide in a Soxlet apparatus for 24 hours. A small quantity of arsenic oxide, which would still remain in the above purified sample, must be reduced by hydrogen current in the pressure indicator itself.

The Filling of the Sample in the Pressure Indicator.

About 10 gr. of the sample was placed into the bulb of a quartz indicator, and a hard glass capillary tube was introduced into the bulb of the indicator, so that the end of the capillary tube was just in the spring of the indicator. Then the indicator was heated from outside by Bunsen burners at 500° C; during the heating of the indicator a current of purified hydrogen was passed into the bulb and its spring through the above mentioned capillary tube, so that a small quantity of arsenic oxide, which still remained in the sample, was at first sublimated and the rest of it reduced to pure arsenic. After a sufficient sublimation in this way, the remainder of the sample in the bulb became perfectly pure brilliant metallic arsenic. Then the indicator was completely evacuated and the bulb of it was sealed up. It was always observed that if arsenic was sublimated in a vacuum, even at room temperature, at first it appeared as the yellow modification, which would be soon transformed into the black modification.

The Furnace of the Pressure Measurement.

A special furnace was constructed for the purpose of keeping the indicator at constant temperature, even at very high temperature. A large iron block of 14 cm. in diameter and of 30 ccm. in height was heated electrically by nichrom wire. In the middle of this iron block, a hole of 3 cm. in diameter and of 25 cm. in depth was

bored, in which the indicator and a thermoelement were placed. This furnace was available till 900°. The temperature of the furnace was measured by a HÉRAEUS platinum-rhodium thermoelement, which was carefully adjusted before the experiment.

The Measurement of the Vapour Pressure.

The method of the pressure measurement by an indicator is exactly the same as that applied by Prof. SMITS and BOKHORST [1]). The equi-

TABLE I. Vapour Pressure of the Solid Phase.

$$\frac{Q}{4.571} = 7357 \qquad C = 8.279$$

t	p atm. (obs.)	Tlogp	$\frac{Q}{4.571}$	$\Delta\left(\frac{Q}{4.571}\right)$	p (calc.)
450	0.026	— 1142	7127	— 230	0.013
500	0.076	— 844	7244	— 113	0.075
525	0.105	— 620	7227	— 130	0.094
550	0.222	— 538	7352	+ 5	0.219
568	0.362	— 371	7334	— 23	0.340
592	0.584	— 202	7363	+ 6	0.598
604	0.785	— 92	7353	— 4	0.777
615.5	0.997	— 2	7357	± 0	0.997
631	1.395	131	7354	— 3	1.387
658	2.392	353	7354	— 3	2.377
665	2.717	401	7365	+ 8	2.729
672	3.035	456	7377	+ 20	3.189
685	3.906	567	7365	+ 8	3.983
697	4.85	664	7368	+ 11	4.96
720.5	6.95	838	7386	+ 29	7.46
741	9.7	999	7396	+ 39	10.6
758	13.3	1157	7378	+ 21	14.0
772	16.9	1281	7371	+ 14	17.4
790	22.3	1432	7368	+ 11	22.8
801	26.1	1522	7370	+ 13	26.9
809	30.0	1595	7363	+ 6	30.2
815	33.6	1662	7348	— 9	33.0

1) loc. cit.

TABLE II. Vapour Pressure of the Liquid Phase.

$$\frac{Q}{4.571} = 2450 \qquad\qquad C = 3.80$$

t	p atm. (obs.)	Tlogp	$\frac{Q}{4.571}$	$\triangle\,\frac{Q}{4.571}$	p (calc.)
808	34.2	1658	2450	$\pm$ 0	34.2
817	35.7	1693	2453	+ 3	35.9
830	38.1	1743	2448	− 2	38.0
843	40.5	1793	2447	− 3	40.2
850	41.6	1818	2449	− 1	41.5
853	42.2	1829	2450	+ 0	42.2

librium between vapour and condensed phase of arsenic is not very quickly established but the heating of the furnace was so slow that there was no difficulty to measure the pressure at any desired temperature. The whole measurement of the vapour pressure of the gray modification of ársenic to its liquid phase, namely from 400° C. to 850° C., required a continuous work of more than 12 hours. The results of the vapour pressure measurement were tabulated as follows: (See Table I, page 389).

Starting from CLAUSIUS and CLAPAYRON's equation and assuming that the heat of vaporization Q, is constant, that the vapour of arsenic follows the gas law and that the volume of the condensed phase can be neglected with respect to that of the vapour, the vapour pressure would be represented by a straight line $T \log p = -\dfrac{Q}{4.571} + CT$.

When the value of $T \log p$, from the observed values of pressure, was plotted against temperature, a good straight line was obtained from 550° C. to 700° C. as shown in Fig. II, from which we can easily calculate $Q/4.571$ and C. The table contains in the last column the values of the pressures calculated from this equation. Above 700° C. however, the $T \log p$—t curve shows some deviation, and the calculated values of $Q/4.571$, assuming C as a constant must deviate. The deviations become gradually smaller as the temperature rises. Some of these deviations may, of course, be experimental errors, because at high temperature a little observation error of temperature would have a great effect on the value of pressure, quite the contrary of the case at low temperature, where a little error in the measurement of pressure, owing to small value of pressure, would have a great effect upon the calculated value of $Q/4.571$. But such a deviation

as observed here depends certainly on the inapplicability of the assumptions which were used in the integration of the CLAUSIUS— CLAPAYRON equation.

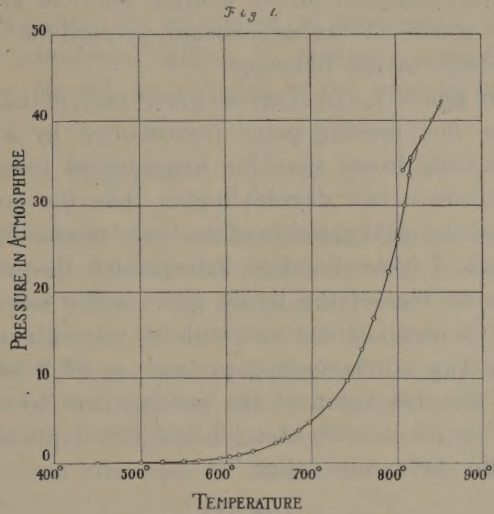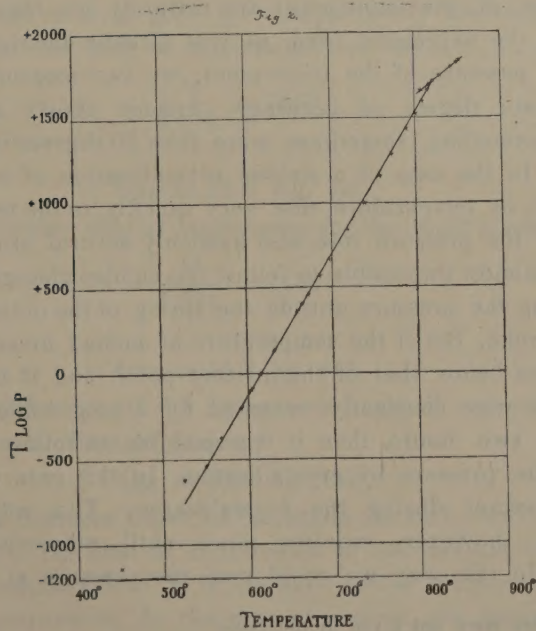In the case of the liquid phase, the observed vapour pressures

Fig. 1.

Fig. 2.

were represented quite well by $T \log p$ plotted against temperature
as a straight line as seen in the table II.

The Melting Point of Arsenic.

The direct measurement of the melting point of arsenic was im-
possible in the course of this experiment, because the thermo-element
was placed outside of the indicator.

As shown in figure I, the observed pressures [1]) of the gray modifica-
tion very near this melting point (represented by a dotted curve)
were always a little lower than the extrapolated pressure curve and
at the temperatures a few degrees higher than the melting point the
indicator showed the right pressure of the liquid phase. For determining
the melting point I have therefore extrapolated the pressure curve of
the solid phase as that of the liquid phase and it was found between
817° C.—818° C. which agreed well with the value given by GOUBEAU[2])
and RASSOW[3]). The corresponding pressure is **35.8** atm. Of course,
we could find also the value of the melting point by the intersection
of the two $T \log p - t$ lines of solid and liquid phases, but in this
case we find the following values.

T	$Q/4.571$	p
822° C.	1710	36.5

These values of the triple-point are certainly too high due to the
deviation of the expression used, as was already mentioned.

As to the pressure of the triple-point, we can measure it directly
with a certain degree of accuracy. Arsenic shows a very large
effect of supercooling, sometimes more than 30 degrees in the authors
experiments. In the case of a sudden crystallisation of such a super-
cooled liquid, its temperature rose very quickly to the melting point;
consequently the pressure rose also suddenly several atmospheres, so
that it was almost impossible to follow this sudden change of the pres-
sure, applying the pressure outside the spring of the indicator so that,
the spring broke. But if the temperature of melted arsenic was kept
a few degrees below that of the melting point, and if the change of
the pressure was constantly watched for a long while, sometimes
longer than two hours, then it was possible to follow the sudden
change of the pressure by crystallisation. In this case the pressure
remained constant during the crystallisation This adjustment of
the pressure, however, requires much skill, otherwise the spring
will break. In this way we could read the pressure at the melting

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[1]) These values were not given in the table.
[2]) loc. cit.

point, which coincided with the value found by the extrapolation of the vapour pressure curve of the solid phase to that of the liquid phase (35,8 atm.).

The Heats of Vaporization and Sublimation of Arsenic.

Heat of vaporization is, of course, a temperature function, but its temperature coefficient dQ/dt is generally negative, so that $T \log p - t$ curve should be concave to the straight line given by the expression

$$T \log p = -\frac{Q}{4.571} + CT$$

which was deduced from the assumption that Q is a constant. On the contrary, the present experimental results show that the $T \log p - t$ curve is somewhat convex to the said expression of pressure, so that we can see that the deviation of the assumption, that Q is a constant, is smaller than the total effect of deviations from other assumptions, so that we may say that the temperature coefficient of the heat of vaporization is comparatively small. It is, therefore, possible to calculate the heat of vaporization from the expression

$$T \log p = -\frac{Q}{4.571} + CT,$$

which was found to hold good for comparatively low temperatures.

For the molecular heat of sublimation we have

$$\frac{Q}{4.571} = 7357$$

hence,

$$Q_{SG} = 33.6 \text{ Kg. cal.}$$

For the molecular heat of vaporization for the liquid phase, we have

$$\frac{Q}{4.571} = 2450$$

hence,

$$Q_{ZG} = 11.2 \text{ kg. cal.}$$

From the difference of the above two heats of vaporization, we have the molecular heat of fusion

$$Q_{SL} = 22.4 \text{ kg. cal.}$$

According to TROUTON's law, LE CHATELIER showed, that the quotient Q/T, where Q is the heat of sublimation at sublimation temperature under one atmosphere and T is the sublimation temperature, would be 30 for all substances. In the case of arsenic, the temperature of sublimation is 616° C. or 889 in absolute unit, then

$$\frac{Q}{T} = \frac{336 \times 10^2}{889} = 37.8.$$

This is a very high abnormal value, just as in the case of phosphorus.

The Black Modification of Arsenic.

It was tried to measure the vapour pressure of the black modification by means of the same indicator as was used in the above experiments. But when the vapour pressure was high enough to measure by this indicator, all the sample in it was transformed into the gray modification [1]), so that it was necessary to find a suitable negative catalyser for this transformation, which would not disturb the pressure measurement. The author hopes to continue this study on a future occasion.

S U M M A R Y.

The vapour pressure of the gray modification of arsenic and its liquid state were measured. From these data, the molecular heat of sublimation, of vaporization and of fusion were calculated.

In conclusion, the author expresses his cordial thanks to Professor A. SMITS for his kind suggestion and for the excellent advice he has given during the work.

Amsterdam, July 15, 1922.

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[1]) LASCHTSCHENKO, (J. chem. Soc., 121. 972 (1922)) gave some remarks on polymorphism of arsenic from the measurement of heat evolved on cooling.

Bio-chemistry. — *"On the Influence of the Composition of the Food on the Calcium output"*. By Prof. B. Sjollema. (Communicated by Prof. H. Zwaardemaker).

(Communicated at the meeting of November 25, 1922).

In my experiments on the influence of cod-liver oil on calcium-, and phosphorus metabolism I found that the economizing effect of cod-liver oil on calcium and on phosphorus, was attended with a decreased production of faeces [1]). The question naturally arose whether, conversely, an augmented production of faeces should result from an increase in the faecal output of calcium and of phosphorus.

The answer to this question is of great importance with regard to our understanding the metabolic phenomena and the physiology of the formation of faeces. The question may be looked at also from a practical point, especially because in experiments with milk-cattle results were repeatedly obtained of late years, which render it highly probable that among the dietetic factors the mineral components are often in the minimum.

In the experiments described below we observed especially the influence of the increase of the quantity of indigestible foodstuffs (ballast) on the calcium- and phosphorus-metabolism. Two ballast-experiments have been performed this summer, both with rabbit III, which since November 1921, was always used for metabolic experiments, and which for chief diet was given a ration of dextrin, lactose, oatstraw boiled with acid and alkali, a calcium-free salt-mixture, a pure protein, viz. casein (afterward partly substituted by gluten of wheat) and a few grammes of butter.

Besides this food-mixture, wheat (whole kernels) was given in the ratio 3 mixture to 1 wheat. In addition almost always 15 grms of cabbage was administered per day. For some weeks the boiled oatstraw was replaced by sawdust boiled with acid and alkali and the cabbage by mangels or carrots.

The calcium-determinations [2]) were made, after destructio of the urine or the faeces, titrimetrically after Mc Crudden, as well as nephelo-

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[1]) Jubilee-Volume Zwaardemaker. Arch. nêerl. de Physiol. t. VII, 1922.

[2]) The analyses were performed by Miss J. E. van der Zande, conservatrix, and by Messrs H. Hooghoudt, analyst and H. Gieteling (volontaire).

metrically after LYMAN. The phosphorus-content was determined (also after destruction) nephelometrically and also colorimetrically, after BELL and DOISY's method altered by Briggs.

Both ballast-experiments consisted of: an initial, and a final period, each of a fortnight, in which the food-mixture contained 3°/₀ ballast; intermediate periods of a week, in which the ballast was raised to 15 °/₀, respectively lowered to 3 °/₀ and the experimental periods proper, each lasting a fortnight. In the first ballast-experiment there were three experimental periods proper, the middle one with an increased protein-content (10°/₀ gluten of wheat) and cystin. During this experiment 40 mgrms of Ca. (as Ca acetate) was given separately per day, but only 15 mgrs in the final period. In the second ballast-test calcium was administered separately to such an amount (at the most 12.7 mgrms per day) that the calcium-content of the food was the same all through the experiment.

As the diet (without cabbage) was composed of 3 parts of the food-mixture and 1 part wheat, it contained less than 15°/₀ oat-straw, viz. $11^{1}/_{4}$ °/₀.

With a heightened percentage of ballast or protein, the procentic amount of dextrin plus lactose in the food-mixture was lowered in both experiments.

The food was always made into a pap with boiling distilled water. The green-fodder, and in other cases the calcium-acetate was administered separately. The animal was weighed every three days. The weight varied from 3530 to 3570 grammes. The average amounts per day of calcium given off in the faeces and present in the food in the various periods of the two ballast-experiments are expressed in mgr. Ca in the following table:

		Initial-period 3 °/₀ ballast	Experimental-period 15 °/₀ ballast	Final-period 3 °/₀ ballast
Output	1st exp.	30.4	88.4 en 69.3	12.5
	2nd exp.	44.1	66.76	21.1
Intake	1st exp.	59.—	76.—	46.3
	2nd exp.	33.6	35.—	36.4

It appears distinctly from both experiments that the calcium-output in the faeces is increased. The ratio of the output in the initial period to that in the experimental period in the first experi-

ment is about 100 : 250; in the second experiment the ratio is about 100 : 150.

That in the one experiment the rise of the calcium-output differed from that in the other, is no doubt due to the very different amounts of calcium administered along with the ingested food.

The extra-ballast in the experimental period as compared with the initial-period (12°/₀ of the fodder-mixture) amounted in the first experiment to about 19 mgrms per day; in the second (when no sawdust plus straw, but only straw was given as ballast) to only 9.4 mgrms. The increase of the faecal calcium-output is therefore, much larger than the amount of calcium present in the extra-ballast. That the calcium in the faeces was only for a small part derived directly from the food is also clear from the fact that especially in the second experiment the faeces contained almost twice the amount of calcium present in the ingested food.

The increase of the amounts of faeces (air-dried) that were produced in the ballast periods, was very large.

The subjoined table gives the production in grammes.

	Initial-periods	Experimental-periods	Final-periods
1st exp.	5.62	11.9 and 10.5	3.35
2nd exp.	3.62	7.72	3.85

The 12 °/₀ extra-ballast in the experimental periods averaged per day in the first experiment about 6,6 grms, in the second 4.7 grms. These values do not differ much from those showing the increments of the faeces production.

In the first experiment the calcium-contents of the faeces (air-dried) were considerably higher during the ballast-periods than in the initial-period; they were lowest in the final-period. (This is most likely due to the smaller quantity of calcium-salts that were administered). In the second experiment the calcium-content of the faeces diminished after the initial-period, which is not surprising if we consider the very great losses and the consequent highly negative balance. In the second experiment the difference between the output and the calcium in the food was about double the difference of the first.

The negative balance is no doubt also answerable for the fact that in the final-period of the second experiment the metabolism of calcium was much more economical than in the initial-period.

Whereas in either period the amount of calcium administered was nearly equal, the output in the initial-period was about three times that of the final-period. When comparing the values of the fore-period and of the experimental period of the second experiment, we see that whereas the quantity of faeces was about the double, the Ca-loss in the faeces was about $1\frac{1}{2}$ times greater than in the initial-period.

The calcium-output via the kidney was in the first experiment during the ballastperiods higher than in the initial- and final-period; in the second experiment there was a gradual decrease of calcium in the urine. This is also most likely attributable to the highly negative balance.

The figures warrant the assumption of a rise of the calcium-output in the urine resulting from a great amount of ballast, if the diet is not too poor in calcium. The quantity of calcium in the faeces was as a rule at least double the quantity of that in the urine.

Regarding the influence of ballast on the phosphorus output we only wish to observe that it was not quite parallel to the influence on the calcium-output. In the ballast-periods the phosphorus-content of the faeces decreased considerably in both experiments.

In a subsequent paper I intend to discuss the nitrogen-, and the iron-outputs in these experiments, and to give the results of the experiments in which we examined the influence of the alkali metals in the food on the calcium- and the phosphorus metabolism.

From the experiments here described it appears:

1. that an increase of the amount of indigestible matter in the food causes a greater loss of calcium via the intestinal canal.

2. that not all the calcium present in the faeces is necessarily derived directly from the food: a large portion of it may be given off by the organism, from which we may conclude that calcium plays a rôle in the production of faeces.

3. that in view of this it is only under certain conditions that an examination of the faeces can show whether in the food or in a part of it (e.g. calcium-salts) calcium occurs in an available form.

4. that in animals, yielding much milk, feeding with much ballast enhances the danger of a negative calcium balance.

(From the Chemical Laboratory of the Utrecht Veterinary University).

Physics. — *"On Heats of Mixing of Normal and Associating Liquids."* By Dr. J. J. van Laar. (Communicated by Prof. H. A. Lorentz).

5. Some Remarks. Before proceeding to the case of anomalous components we will make a few remarks.

a). So far we have always written n_1 and n_2 for the molecule values. But often $n_1 = 1 - x$ and $n_2 = x$ is put, so that $n_1 + n_2 = 1$. The differential quotients of w with respect to n_1 and n_2 can then also be calculated by the differential quotient with respect to x by means of the equations

$$w_1 = \frac{\partial \omega}{\partial n_1} = w - x \frac{\partial \omega}{\partial x} \quad ; \quad w_2 = \frac{\partial \omega}{\partial n_2} = w + (1-x) \frac{\partial \omega}{\partial x} .$$

This immediatdly follows from $w = n_1 w_1 + n_2 w_2$ and

$$\frac{\partial \omega}{\partial x} = \frac{\partial \omega}{\partial n_1} \frac{dn_1}{dx} + \frac{\partial \omega}{\partial n_2} \frac{dn_2}{dx} = -\frac{\partial \omega}{\partial n_1} + \frac{\partial \omega}{\partial n_2} = -w_1 + w_2,$$

The same thing, of course, holds not only for w, but for every homogeneous function of the 1st degree with respect to the molecular values n_1 and n_2 (e.g. v).

For a homogeneous function of the 0th degree with respect to n_1 and n_2 (e.g. w_1, v_1, etc.; the degree of dissociation of the double molecules β (see further), etc.) we have:

$$\frac{\partial \beta}{\partial n_1} = -x \frac{\partial \beta}{\partial x} \quad ; \quad \frac{\partial \beta}{\partial n_2} = (1-x) \frac{\partial \beta}{\partial x},$$

which follows from:

$$n_1 \frac{\partial \beta}{\partial n_1} + n_2 \frac{\partial \beta}{\partial n_2} = 0 \quad \text{and} \quad \frac{\partial \beta}{\partial x} = -\frac{\partial \beta}{\partial n_1} + \frac{\partial \beta}{\partial n_2} \text{ (see above)}.$$

b). We have seen that when $v_1{}^\bullet \sqrt{a_2} - v_2{}^\bullet \sqrt{a_1} = 0$ (i.e. when the critical pressures of the two components are the same) Δv becomes $= 0$ according to (3) (hence also Δv_1 and Δv_2). But according to (1) then also $w = 0$ (and this holds also for w_1 and w_2).

Now

$$v = v_0 + \Delta v = n_1 v_1{}^\circ + n_2 v_2{}^\circ + \Delta v,$$

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hence when $\Delta v = 0$, simply:

$$v = n_1 v_1^0 + n_2 v_2^0 \quad ; \quad v_1 = \frac{\partial v}{\partial n_1} = v_1^0 \quad ; \quad v_2 = \frac{\partial v}{\partial n_2} = v_2^0,$$

so that then v becomes a *linear* function of x, viz. $v = v_1^0 + x(v_2^0 - v_1^0)$.

In the supposed case also the following equation may be written (see § 2):

$$\frac{a}{v} = \frac{a}{v_s} = n_1 \frac{a_1}{v_1^0} + n_2 \frac{a_2}{v_2^0},$$

hence also

$$T_k = n_1 T_{k_1} + n_2 T_{k_2},$$

i.e. the *critical temperature* of the "ideal" mixture is also a *linear* function of x, viz. $T_k = T_{k_1} + x(T_{k_2} - T_{k_1})$.

For a/v^2 holds:

$$\frac{a}{v^2} = \frac{a}{v_s^2} = \frac{(n_1 \sqrt{a_1} + n_2 \sqrt{a_2})^2}{(n_1 v_1^0 + n_2 v_2^0)^2} = \frac{a_1}{v_1^{0^2}} = \frac{a_2}{v_2^{0^2}},$$

when $\sqrt{a_1}/v_1^0$ is $= \sqrt{a_2}/v_2^0$ in consequence of the equality of the critical pressures. In ideal mixtures the *critical pressure* remains, therefore, constant $= p_{k_1} = p_{k_2}$, whatever is the value of x.

6. Associated components.

For the calculation of w we can adopt the whole derivation of § 2 unchanged; it should only be borne in mind that, the degree of dissociation of the double molecules of the components being β_1 and β_2 in the mixture, that of the *pure* components will be different, viz. β_1^0 and β_2^0. Thence

$$(n_1 e'_1 + n_2 e'_2) - (n_1 e'_1 + n_2 e'_2)_0$$

will not be $= 0$ now. For we can write e.g.

$$e_1' = \frac{1-\beta_1}{2}(e_1')_d + \beta_1 (e_1')_e = (e_1')_{\frac{1}{2}d} + \beta_1 \{(e_1')_e - (e_1')_{\frac{1}{2}d}\} = (e_1')_{\frac{1}{2}d} + \beta_1 q_1,$$

when $(e'_1)_d$ is the energy constant of a double molecule and $(e'_2)_e$ of a single molecule. A similar expression applies to e'_2. Here e'_1 and e'_2 always refer, therefore, to single molecular quantities. The quantities q_1 and q_2 are the "pure" heats of dissociation, i.e. without the parts referring to the volume contraction (see further below). For the above expression the following equation may, therefore, be written:

$$n_1 (\beta_1 - \beta_1^0) q_1 + n_2 (\beta_2 - \beta_2^0) q_2 = q.$$

Further it should be borne in mind that a remains unchanged on dissociation, for on simple joining of two single molecules to one double molecule, $\sqrt{a}$ will likewise become twice as great;

hence $\sqrt{a}$ will have the same value for $1/2$ double molecule as for 1 single molecule.

The same thing is assumed with regard to the heat capacities k_1 and k_2. There too — especially for larger molecules — no contraction of the value is supposed.

Thus instead of (1) the following form is found:

$$w = q + n_1 n_2 \frac{(v_2^0 \sqrt{a_1} - v_1^0 \sqrt{a_2})^2}{v_0\, n_1^0\, v_2^0} + \left(p + \frac{a}{v\,v_0}\right)\Delta v \quad . \quad (1_{ass.})$$

The values of w_1 and w_2 are found in an entirely analogous way as in § 2, viz. from (cf. equation (1^a)):

$$w = q + n_1 n_2 \frac{(v_2\sqrt{a_1} - v_1\sqrt{a_2})^2}{v\,v_1\,v_2} + \left(p + \frac{a_1}{v_1 v_1^0}\right)n_1\Delta v_1 + \left(p + \frac{a_2}{v_2 v_2^0}\right)n_2 \Delta v_2,$$

in which further:

$$\frac{a_1}{v_1 v_1^0}\,\Delta v_1 = \frac{a_1}{(v_1^0)_{\beta_1^0}} - \frac{a_1}{(v_1)_{\beta_1}} = \left(\frac{a_1}{(v_1^0)_{\beta_1^0}} - \frac{a_1}{(v_1)_{\beta_1^0}}\right) + \left(\frac{a_1}{(v_1)_{\beta_1^0}} - \frac{a_1}{(v_1)_{\beta_1}}\right) =$$

$$= \frac{a_1}{(v_1^0 v_1)_{\beta_1^0}}(v_1 - v_1^0)_{\beta_1^0} + \frac{a_1}{(v_1)_{\beta_1^0}(v_1)_{\beta_1}}(\beta_1 - \beta_1^0)\,\Delta_1,$$

as

$$v_1 = \frac{1-\beta_1}{2}(v_1)_d + \beta_1 (v_1)_e = (v_1)_{1/2 d} + \beta_1\left((v_1)_e - (v_1)_{1/2 d}\right) = (v_1)_{1/2 d} + \beta_1\,\Delta_1,$$

so that $(v_1)_{\beta_1} - (v_1)_{\beta_1^0} = (\beta_1 - \beta_1^0)\,\Delta_1$. In this Δ_1 represents the change of volume (contraction), when *in* the mixture $1/2$ double molecule becomes 1 single molecule.

This quantity Δ_1 can possess a considerable value. The phenomenon of the *maximum-density* of *water* e.g. finds its explanation in the great value of Δ_1, so that below $4°$ C. the thermal expansion is even exceeded by the *diminution* of volume in consequence of the progressing dissociation of the double molecules. Above $4°$ C. the thermal expansion will predominate [1]).

The same thing holds for $\dfrac{a_2}{v_2 v_2^0}\,\Delta v_2$, so that, taking into account that also

$$\left.\begin{aligned}
\Delta v_1 &= (v_1)_{\beta_1} - (v_1^0)_{\beta_1^0} = (v_1 - v_1^0)_{\beta_1^0} + \left((v_1)_{\beta_1} - (v_1)_{\beta_1^0}\right) = (\Delta v_1)_{\beta_1^0} + (\beta_1 - \beta_1^0)\Delta_1 \\
\Delta v_2 &= (v_2)_{\beta_2} - (v_2^0)_{\beta_2^0} = (v_2 - v_2^0)_{\beta_2^0} + \left((v_2)_{\beta_2} - (v_2)_{\beta_2^0}\right) = (\Delta v_2)_{\beta_2^0} + (\beta_2 - \beta_2^0)\Delta_2
\end{aligned}\right\},$$

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[1]) This explanation, given by me for the first time in the VAN 'T HOFF-volume of the Zeitschr. f. ph. Ch. (Bd. **31**, 1899, p. 1 et seq.)) more than 20 years ago (see particularly p. 12 –16), is not yet found mentioned in any handbook. Except for a few favourable exceptions this is also the case with many other theories, rules and explanations given by me.

we may finally write:

$$w = n_1(\beta_1 - \beta_1^\circ)\left[q_1 + \left(p + \frac{a_1}{(v_1)_{\beta_1^\circ}(v_1)_{\beta_1}}\right)\Delta_1\right] +$$

$$+ n_2(\beta_2 - \beta_2^\circ)\left[q_2 + \left(p + \frac{a_2}{(v_2)_{\beta_2^\circ}(v_2)_{\beta_2}}\right)\Delta_2\right] + n_1 n_2 \frac{(v_2\sqrt{a_1} - v_1\sqrt{a_2})^2}{v\, v_1\, v_2} +$$

$$+ \left(p + \frac{a_1}{(v_1 v_1^\circ)_{\beta_1^\circ}}\right) n_1\, (\Delta v_1)_{\beta_1^\circ} + \left(p + \frac{a_2}{(v_2 v_2^\circ)_{\beta_2^\circ}}\right) n_2\, (\Delta v_2)_{\beta_2^\circ}$$

In this the quantities

$$Q_1 = q_1 + \left(p + \frac{a_1}{(v_1)_{\beta_1^\circ}(v_1)_{\beta_1}}\right)\Delta_1 \quad ; \quad Q_2 = q_2 + \left(p' + \frac{a_2}{(v_2)_{\beta_2^\circ}(v_0)_{\beta_2}}\right)\Delta_2$$

are the *total* (absorbed) heats of dissociation of the components in the mixture, on transition of $^1/_2$ double molecule to 1 single molecule. When we further write:

$$n_1\, (\beta_1 - \beta_1^\circ)\, Q_1 + n_2\, (\beta_2 - \beta_2^\circ)\, Q_2 = Q,$$

we get finally:

$$w = Q + n_1 n_2 \frac{(v_2\sqrt{a_1} - v_1\sqrt{a_2})^2}{v\, v_1\, v_2} + \left(p + \frac{a_1}{(v_1 v_1^\circ)_{\beta_1^\circ}}\right) n_1 (\Delta v_1)_{\beta_1^\circ} +$$
$$+ \left(p + \frac{a_2}{(v_2 v_2^\circ)_{\beta_2^\circ}}\right) n_2\, (\Delta v_2)_{\beta_2^\circ} \qquad (1^a_{ass.})$$

Taking the same remark into consideration in the differentiation as in § 2, we find from this for w_1 and w_2:

$$w_1 = \left[(\beta_1 - \beta_1^\circ)Q_1 + n_1 Q_1 \frac{d\beta_1}{dn_1} + n_2 Q_2 \frac{d\beta_2}{dn_1}\right] + n_2^2 \frac{(v_2\sqrt{a_1} - v_1\sqrt{a_2})^2}{v^2 v_1} +$$
$$+ \left(p + \frac{a_1}{(v_1 v_1^\circ)_{\beta_1^\circ}}\right)(\Delta v_1)_{\beta_1^\circ}$$

$$w_2 = \left[(\beta_2 - \beta_2^\circ)Q_2 + n_1 Q_1 \frac{d\beta_1}{dn_2} + n_2 Q_2 \frac{d\beta_2}{dn_2}\right] + n_1^2 \frac{(v_2\sqrt{a_1} - v_1\sqrt{a_2})^2}{v^2 v_2} +$$
$$+ \left(p + \frac{a_2}{(v_2 v_2^\circ)_{\beta_2^\circ}}\right)(\Delta v_2)_{\beta_2^\circ} \qquad (2_{ass})$$

In the equation $(1_{ass.})$ we now have (see above):

$$\Delta v = v - v_0 = n_1\Delta v_1 + n_2\Delta v_2 = n_1(\Delta v_1)_{\beta_1^\circ} + n_2(\Delta v_2)_{\beta_2^\circ} +$$
$$+ n_1\,(\beta - \beta_1^\circ)\,\Delta_1 + n_2\,(\beta_2 - \beta_2^\circ)\,\Delta_2 \qquad , \quad (8)$$

in which the last two terms with Δ_1 and Δ_2 will be greatly predominant. Even if the critical pressures of the two components were about the same, so that $(\Delta v_1)_{\beta_1^\circ}$ and $(\Delta v_2)_{\beta_2^\circ}$ will become $= 0$,

Δv will remain comparatively great, because Δ_1 and Δ_2 will retain their values.

Hence in associating components the term with Δv will still more greatly predominate in $(1_{ass.})$ than in mixtures of normal substances, because also q_1 and q_2 will never be great. Just as with the capacities of heat, these differences in the energy constants of the half double molecules and of the single molecules will probably be even quite negligible. Even more than for non-associated components now

$$\frac{w}{\Delta v} = p + \frac{a}{vv_0} = \frac{a}{vv_0} = \frac{a}{v^2}$$

may be put, which values will again not differ much in different pairs of substances, when the critical pressures of these substances do not differ too much.

7. Approximative value of $\beta_1 - \beta_1^{\,0}$ with small values of n_1 (or x).

From the perfectly accurate equation of dissociation [1]) of the 1st component in the mixture, viz.:

$$\frac{(1-x)\,\beta_1^{\,2}}{^1/_2\,(1-\beta_1)\left[(1-x)\frac{1+\beta_1}{2} + x\frac{1+\beta_2}{2}\right]} = K_1 = \frac{K'_1}{p + a/v^2}\,e^{-\frac{p+a/v^2}{RT}\Delta_1},$$

in which K'_1 is still a function of the temperature, or also

$$\frac{\beta_1^{\,2}}{(1-\beta_1^{\,2})\left(1 + \frac{x}{1-x}\frac{1+\beta_2}{1+\beta_1}\right)} = \frac{1}{4}K_1 \quad , \quad \text{i. e.} \quad \frac{\beta_1^{\,2}}{1-\beta_1^{\,2}} = \frac{1}{4}K_1(1+\varphi),$$

when $\dfrac{x}{1-x}\dfrac{1+\beta_2}{1+\beta_1} = \varphi$ is put, follows immediately:

$$\beta_1 = \sqrt{\frac{^1/_4\,K_1(1+\varphi)}{1 + ^1/_4\,K_1(1+\varphi)}} = \sqrt{\frac{^1/_4\,K_1}{1 + ^1/_4\,K_1}}\sqrt{\frac{1+\varphi}{1 + \frac{^1/_4\,K_1}{1 + ^1/_4\,K_1}\varphi}}.$$

Here is evidently $\sqrt{\dfrac{^1/_4\,K_1}{1 + ^1/_4\,K_1}} = \beta_1^{\,0}$ (for $\varphi = 0$ when $x = 0$); hence

$$\beta_1 = \beta_1^{\,0}\sqrt{\frac{1+\varphi}{1 + \beta_1^{\,0^2}\varphi}},$$

[1]) See among other things Arch. Teyler XI, 3e Partie, 1908, p. 44 et seq.

which for smaller values of x (φ) passes into

$$\beta_1 = \beta_1^{\,\circ}\,(1 + {}^1/_2\,(1 - \beta_1^{\,\circ\,2})\,\varphi),$$

so that we get:

$$\beta_1 - \beta_1^{\,\circ} = {}^1/_2\,\beta_1^{\,\circ}\,(1 - \beta_1^{\,\circ\,2})\,\varphi = {}^1/_2\,\beta_1^{\,\circ}\,(1 - \beta_1^{\,\circ\,2})\,\frac{x}{1-x}\,\frac{1+\beta_2}{1+\beta_1}.$$

Now for small values of x we may put $\beta_2 = 1$ and $\beta_1 = \beta_1^{\,\circ}$, so that finally becomes in approximation:

$$(x \text{ small}) \quad \beta_1 - \beta_1^{\,\circ} = \frac{x}{1-x}\,\beta_1^{\,\circ}\,(1 - \beta_1^{\,\circ})\,;\;\cdots \quad . \quad . \quad . \quad . \quad (9)$$

and $x\,\beta_1^{\,\circ}(1 - \beta_1^{\,\circ})$ may be written for $n_1(\beta_1 - \beta_1^{\,\circ}) = (1-x)\,(\beta_1 - \beta_1^{\,\circ})$.

8. Reduction of the formula for w in normal components.

When we want to test the formulae derived above by some experimental data, we can only do so with mixtures of *normal* components. With regard to *anomalous* components (water, alcohol, acids, etc.) we lack the knowledge of the quantities q and Δ. On the contrary we calculated them approximately at the time (loc. cit.) from the experimental results, e.g. from the volume-contraction of water-alcohol mixtures. We must, therefore, confine ourselves, to formulae (1) and (3), and when we apply these also to abnormal components, we shall be able to find something regarding the probable values of q and Δ from the *deviations* between the calculated values and those found experimentally.

For Δv we found (cf. besides (3), also (3^a) and (3^b)):

$$\Delta v = n_1 n_2 \frac{{}^2/_7\,m}{1 - {}^2/_7\,m}\,\frac{v_1^{\,\circ}\sqrt{a_2}(1-\tau)}{a_1 a_2}\left\{(\sqrt{a_1} - \sqrt{a_2})\sqrt{a_1 a_2} - \frac{1}{2}\,(n_1 a_1 + n_2 a_2)\frac{v_1^{\,\circ}\sqrt{a_2}}{v_0}(1-\tau)\right\},$$

when

$$\frac{v_2^{\,\circ}\sqrt{a_1}}{v_1^{\,\circ}\sqrt{a_2}} = \frac{b_{k_2}\sqrt{a_{k_1}}}{b_{k_1}\sqrt{a_{k_2}}} = \sqrt{\frac{p_{k_1}}{p_{k_2}}} = \tau$$

is written. Therefore, according to (1), with omission of p, w becomes:

$$w = n_1 n_2\left[\frac{v_1^{\,\circ\,2} a_2}{v_0\,v_1^{\,\circ}\,v_2^{\,\circ}}\,(1-\tau)^2 + \frac{a}{v\,v_0}\frac{{}^2/_7\,m}{1 - {}^2/_7\,m}\,\frac{v_1^{\,\circ}\sqrt{a_2}\,(1-\tau)}{a_1 a_2}\right\}\quad \Big\}\Big],$$

or also

$$w = n_1 n_2\,\frac{a_2}{v_2^{\,\circ}}\frac{v_1^{\,\circ}}{v_0}\left[(1-\tau)^2 + \frac{1}{6}\,(1-\tau)\frac{a}{a_2}\frac{v_2^{\,\circ}}{v}\left\{\left(1 - \sqrt{\frac{a_2}{a_1}}\right) - \frac{1}{2}\left(n_1 + n_2\frac{a_2}{a_1}\right)\frac{v_1^{\,\circ}}{v_0}(1-\tau)\right\}\right],$$

when in approximation $m = T : T_k = \frac{1}{2}$ is put. When $7 R T_{k_2}$ is written for $a_2/v_2{}^0$ and $7 R T_k$ for a/v, and further

$$\frac{a_2}{a_1} = \frac{a_{k_2}}{a_{k_1}} = \frac{b_{k_2}}{b_{k_1}} \frac{T_{k_2}}{T_{k_1}} = \varphi,$$

in which $b_{k_2} : b_{k_1}$ can be calculated from $(T_{k_2} : p_{k_2}) : (T_{k_1} : p_{k_1})$, we get finally:

$$w = 7\, n_1 n_2\, R T_{k_2} \frac{v_1{}^0}{v_0}\left[(1-\tau)^2 + \right.$$
$$\left. + \frac{1}{6} \frac{T_k}{T_{k_2}}(1-\tau) \left\{(1-\sqrt{\varphi}) - \frac{1}{2}\frac{v_1{}^0}{v_0}(1-\tau)(n_1+n_2\,\varphi)\right\}\right] . (10)$$

When *equimolecular* quantities of the components are used, $n_1 = 1 - x = \frac{1}{2}$ and also $n_2 = x = \frac{1}{2}$, and we get:

$$w_{\frac{1}{2}} = \frac{7}{4} R T_{k_2} \frac{v_1{}^0}{\frac{1}{2}(v_1{}^0 + v_2{}^0)}\left[(1-\tau)^2 + \right.$$
$$\left. + \frac{1}{6}\frac{\frac{1}{2}(T_{k_1}+T_{k_2})}{T_{k_2}}(1-\tau)\left\{(1-\sqrt{\varphi}) - \frac{1}{4}\frac{v_1{}^0}{\frac{1}{2}(v_1{}^0+v_2{}^0)}(1-\tau)(1+\varphi)\right\}\right],$$

as $v_0 = n_1 v_1{}^0 + n_2 v_2{}^0$, and approximately $T_k = \frac{1}{2}(T_{k_1} + T_{k_2})$. The latter is strictly accurate only when the critical pressures of the two components are equal (see § 5 under *b*). When by way of abbreviation

$$\frac{v_1{}^0}{\frac{1}{2}(v_1{}^0 + v_2{}^0)} = \lambda_1 \quad ; \quad \frac{\frac{1}{2}(T_{k_1}+T_{k_2})}{T_{k_2}} = \lambda_2$$

is put, then finally with $R = 2$, so that w is expressed in gr. kal.:

$$w_{\frac{1}{2}} = \frac{7}{2}\, \lambda_1 T_{k_2}\left[(1-\tau)^2 + \frac{1}{6}\lambda_2(1-\tau)\left\{(1-\sqrt{\varphi}) - \frac{1}{4}\lambda_1(1-\tau)(1+\varphi)\right\}\right]. \ (10^a)$$

This formula is, of course, asymmetrical on account of T_{k_2} only *in appearance*, in as much as we have placed $v_1{}^0 \sqrt{a_2}$ in $v_1{}^0 \sqrt{a_2} - -v_2{}^0 \sqrt{a_1}$ outside the parentheses. If we had done this with $v_2{}^0 \sqrt{a_1}$ T_{k_1} would have appeared as fore-factor, but then $\sqrt{(p_{k_1} : p_{k_2})}-1$ would also have been substituted for $1-\sqrt{(p_{k_2} : p_{k_1})}$. We now henceforth take τ always < 1, so that that component is chosen as the first, of which the critical pressure is *lowest*.

In consequence of the fore-factor $R T_{k_2} = \frac{1}{7} a_2/v_2{}^0$, w is duly of the dimensions of an energy. Further only *ratios* of quantities occur in (10^a). If, therefore, the components belong to the same family of substances, e.g. to the extensive family of "ordinary" substances (critical temp. between $400°$ and $600°$ abs., $\gamma = 0,9$, $f = 7$, $r = v_k : b_k = 2,1$, etc.), the error committed by putting $v_2{}^0 : v_1{}^0 = = b_{k_2} : b_{k_1}$ and $a_2 : a_1 = a_{k_2} : a_{k_1}$ in τ and φ, is certainly negligible.

For the ratios in question are about the same for all these sub-
stances — provided only that they be in corresponding states (e.g.
$m = \frac{1}{2}$) — which will approximately be the case when the critical
temperatures are not too divergent. Only in the fore-factor $a_2/v_2{}^0$
care has of course been taken by means of the factor 7 that the
corrections in question are duly observed [1]).

As according to (1)

$$w = \Delta P + \frac{a}{v\, v_\bullet} \Delta v = \Delta P + \frac{a}{v_\bullet} \frac{\Delta v}{v} = \Delta P + 7R \cdot \tfrac{1}{2} (T_{k_1} + T_{k_2}) \frac{\Delta v}{v}$$

(see above), it immediately follows from (10^a) that

$$\frac{\Delta v_{\frac{1}{2}}}{v} = \frac{1}{24} \lambda_1 (1-\tau) \left\{ (1 - \sqrt{\varphi}) - \frac{1}{4} \lambda_1 (1-\tau) (1+\varphi) \right\}, \quad (11)$$

from which $\Delta v_{\frac{1}{2}}$ can be calculated $(v = 1)$.

When the critical pressures of the two components are equal,
then τ is $= 1$ and w and Δv both become $= 0$. As we already
pointed out in our first paper, then (i.e. with very small difference
of p_{k_1} and p_{k_2}) $1-\tau$ is greater than $(1-\tau)^2$, so that the part with
Δv will predominate in w. But if the critical pressures differ some-
what more, the first part will continue to predominate. As will
appear from the calculation in the following paragraph, the part
with Δv is at most $\frac{1}{5}$ of the first part, but often it is much less.
Hence the principal term of w remains ΔP, and this may be repre-
sented by the single formula $(x = \frac{1}{2})$:

$$w_{\frac{1}{2}} \smile \Delta P_{\frac{1}{2}} = \frac{7}{2} \lambda_1 T_{k_2} (1-\tau)^2.$$

If one wants, therefore, to form an approximate idea of the value
of the heat of mixing w, it will mostly be sufficient to calculate
the said value of ΔP.

The value of Δv will sometimes be positive, sometimes negative.
Not always are the conditions for contraction (Δv negative) fulfilled
— see § 3: "As regards the sign of Δv" etc. According to the
tables on p. 160—161, 169 and 176 of KREMANN's cited book there
are about an equal number of mixtures of normal liquids with
a positive as with a negative Δv. Everything, of course, depends on
whether

$$(1 - \sqrt{\varphi}) - \frac{1}{4} \lambda_1 (1-\tau) (1+\varphi) > \text{ of } < 0,$$

---

[1]) As $RT_k = \frac{8}{27} \lambda \, a_k{}^i/b_k$ in which λ is about $\frac{27}{28}$ for ordinary substances,
$a_k/b_k = \frac{7}{2} RT_k$. Now a at $T = \frac{1}{2} T_k$ is about $1.4\, a_k$ and $v = 0.73\, b_k$, so that
we have $a/v = 2\, a_k/b_k = 7 RT_k$.

i. e. whether (in approximation) $\sqrt{\varphi}$ is $<$ or $>1-\frac{1}{2}\lambda_1(1-\tau)$. And, of course, nothing can be said beforehand with regard to this.

9. Some numerical results.

That in case of mixing of normal substances the heat of mixing is actually $=0$ or very slight ($+$ or $-$), when the *critical pressures are about equal*, appears among others from the following examples (compare also Table V on p. 64—65 in KREMANN's book).

$$C_6H_5Cl - C_6H_5Br \qquad (p_k = 44,6 \text{ and } 44,6) | w=0 \text{ to } 3,3 (\text{YOUNG } 1903 \text{ and KR.})$$

Dimethylaniline— m. Xylene	(„ » 35,8 » 35,8)	$+$ 2,8	
Amylformiate — Propylacetate	(» » 34,1 » 34,8)	$-$ 2,0	KREMANN C.S.
p-Xylene — m-Xylene	(» » 35,0 » 35,8)	$-$ 2,0	1914.
p-Xylene — o-Xylene	(» » 35,0 » 36,9)	$+$ 2,3	
m-Xylene – o-Xylene	(» » 35,8 » 36,9)	$+$ 2,0	

Of the many mixtures studied, of which the critical pressures are more or less different, we have calculated [1]) the following ones according to (10^a) for a comparison with the results of the observation.

1. Toluene-Benzene. Here we have:

p_k	T_k	$T_k/p_k = \theta b_k$	$T_k \cdot \theta b_k$	τ	φ	$\sqrt{\varphi}$	λ_1	λ_2
41.6	594	14.3	8490	0.932	0.774	0.880	1.10	1.028
47.9	562	11.7	6580					

For the calculation of $\lambda_1 = v_1^0 : \frac{1}{2}(v_1^0 + v_2^0)$ we may either take the densities at the temperature of the experiment, or — as v_1^0 and v_2^0 will be proportional to b_{k_1} and b_{k_2} — introduce the above values of θb_k (θ is a certain numerical value). We have done the latter. We now find:

$$w = {}^7 ._2 \times 1,1 \times 562 (0,00462 + \frac{1}{6}1,03 . 0,068 \{0,120 - \frac{1}{4}1,1 . 0,068 . 1,744 \})$$
$$= 2162 (0,00462 + 0,0117 \{0,120 - 0,033 \})$$
$$= 2162 (0,00462 + 0,00102) = 2162 \times 0,00564 = \mathbf{12,2} \text{ gr.cal.}$$

ALEXEJEW found 14,0 (from YOUNG follows 15,8, and KR. found 18,9).

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[1]) Both in Table 5 for w (on p. 164) and in Table 23 for Δv (p. 175) the "calculated" values in KREMANN's book are all inaccurate, because instead of the accurate formula derived by me for Δv, an approximate one was used. Besides $\frac{27}{8} RT_c$ was put in w instead of $a/v = a/b = 7RT_c$, which in itself already causes the values calculated for w to be twice too small. Etc.

It is seen that here the value of the term Δv is about $22°/_0$ of the principal term.

The discrepancies between calculated and found values — also in the following examples — must be chiefly ascribed, besides to experimental difficulties and small approximations in the derivation of the formula, to the often inaccurately known values of the *critical pressures*. Even a slight error in them gives already rise to a comparatively great change in the value of $(1-\tau)^2$.

The following value is immediately found for $\Delta v/_v$ according to (11):

$$\Delta v/_v = {}^1/_{24} \times 1{,}1 \times 0{,}068 \times 0{,}087 = \mathbf{0{,}00027}.$$

The value $0{,}05 : 100 = 0{,}00050$ was found (see Table 21 on p. 160—161 and p. 175 in KR.) [1]).

2. **Metaxylene-Benzene**. There we have what follows.

p_k	T_k	θb_k	$T_k \cdot id.$	τ	φ	$\sqrt{\varphi}$	λ_1	λ_2
35.8	622	17.4	10820	0.864	0.608	0.780	1.20	1.053
47.9	562	11.7	6580					

This gives:

$w = {}^7/_2 \times 1{,}2 \times 562 (0{,}0185 + {}^1/_6 \, 1{,}05 \cdot 0{,}136 \{0{,}220 - {}^1/_4 1{,}2 \cdot 0{,}136 \cdot 1{,}608\})$

$= 2351 \, (0{,}0185 + 0{,}0239 \{0{,}220 - 0{,}065\})$

$= 2351 \, (0{,}0185 + 0{,}0037) = 2351 \times 0{,}0222 = \mathbf{52{,}2}$ gr. cal.

KREMANN found 57 gr. cal. The agreement is again very satisfactory (taking the above remarks into consideration). The term with Δv is $20°/_0$ of the principal term. Further:

$$\Delta v/_v = {}^1/_{24} \times 1{,}2 \times 0{,}136 \times 0{,}155 = \mathbf{0{,}00105}.$$

KR. found $0{,}15 : 100 = 0{,}00150$. The order of magnitude is the same in every case.

The mixtures with CCl_4 as component all present deviations. Now CCl_4 is certainly *associated* (see also KR., p. 68 and 140), so that this accounts for the deviations.

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[1]) It is not very clear in KREMANN's records whether we should divide by 100, or by ${}^1/_2 \, (v_1{}^0 + v_2{}^0) = 195{,}5$. (Cf. p. 175). In the latter case $\Delta v/_v$ would be $= 0{,}00026$, in perfect agreement with the calculated value. As regards YOUNG's value, it deviates considerably from that of KREMANN. He found viz. $0{,}16°/_0$ instead of $0{,}05°/_0$, hence more than 3 times the value. Also for w there are often large differences.

Thus according to calculation the mixture $CCl_4 — C_6H_6$ ($p_k = 45,0$ and 47,9) would have to give a heat of mixing $= + 2,0$ gr. cal., whereas $+ 21,4$ was found by YOUNG. The value of $\Delta v/v$, viz. $— 0,00130$, found by YOUNG, points to a pretty great volume contraction which, however, does not account for the too great positive value for w. Also the vapour-tension line deviates here.

The mixture $C_7H_8 — CCl_4$ ($p_k = 41,6$ and 45,0) leads us to expect $+ 3,9$ for w, whereas w is $= — 8,5$ according to YOUNG. To this belongs $\Delta v/v = — 0,00070$ according to the same author, and accordingly w and Δv are both negative.

3. $C_2H_4Ac — CCl_4$. The calculation of this mixture may be reproduced here. We have:

p_k	T_k	θb_k	$T_k . id.$	τ	φ	$\sqrt{\varphi}$	λ_1	λ_2
38.0	523.2	13.77	7204	0.9189	0.9543	0.9769	1.054	0.9704
45.0	556.2	12.36	6875					

giving:

$w = {}^7/_2 \times 1,054 \times 556,2 (0,006577 +$
$\qquad + {}^1/_6 0,9704 . 0,0811 \{0,0231 — {}^1/_4 1,054 . 0,0811 . 1,9543\})$
$= 2052 (0,006577 + 0,01312 \{0,0231 — 0,0418\})$
$= 2052 (0,006577 — 0,000245) = 2052 \times 0,006332 = + \mathbf{13,0}$ gr. cal.

YOUNG found $— 20,1$. Calculation here gives a negative value for Δv, the correction term not being even so much as $4°/_0$ of the principal term. For $\Delta v/v$ we calculate:

$$\Delta v/v = {}^1/_{24} \times 1,054 \times 0,0811 \times (— 0,187) = — \mathbf{0,00067}.$$

The value $+ 0,00030$ was found by YOUNG. Again w and Δv (found) have opposed signs, which is strange, and renders the accuracy of YOUNG's values somewhat questionable. (Cf. also the last Footnote).

Let us now give a few examples of recognized *associated* components.

4. $C_6H_6 — C_2H_5OH$. We have in this case:

p_k	T_k	θb_k	$T_k . id.$	τ	φ	$\sqrt{\varphi}$	λ_1	λ_2
47.9	561.6	11.72	6582	0.8720	0.6427	0.8017	1.177	1.044
63.0	516.2	8.194	4230					

from which follows:

$w = \frac{7}{2} \times 1{,}177 \times 516{,}2\,(0{,}01638 +$

$\qquad\qquad + \frac{1}{6}\,1{,}044 \cdot 0{,}1280\,\{0{,}1983 - \frac{1}{4}\,1{,}177 \cdot 0{,}1280 \cdot 1{,}6427\})$

$\quad = 2126\,(0{,}01638 + 0{,}02227\,\{0{,}1983 - 0{,}0619\})$

$= 2126\,(0{,}01638 + 0{,}00304) = 2126 \times 0{,}01942 = \mathbf{41{,}3}$ gr. cal.

But $+120$ is found (YOUNG). [WINKELMANN (1872) gives -110]. The term with Δv is here 19% of the principal term. We calculate for $\Delta v / v$:

$$\Delta v / v = \frac{1}{24} \times 1{,}117 \times 0{,}1280 \times 0{,}1364 = \mathbf{0{,}00086}.$$

YOUNG found 0, and GUTHRIE $+$ (1884).

In the expression $\Delta v = (\Delta v)_{norm} + \frac{1}{2}\,(\beta_2 - \beta_2^{\,0})\,\Delta_2$ (cf. (8) in § 6) Δ_2, i. e. the volume contraction on transition of 1 double molecule C_2H_5OH to two single molecules, seems therefore to have a small negative value. But in $w = w_{norm} + Q = w_n + \frac{1}{2}\,(\beta_2 - \beta_2^{\,0})\,Q_2 =$

$= w_n + \frac{1}{2}(\beta_2 - \beta_2^{\,0})\left(q_2 + \dfrac{a_2}{(v_2)_{\beta_2^0}\,(v_2)_{\beta_2}}\,\Delta_2\right)$ (cf. e. g. $1^a_{ass.}$ in § 6) Q_2 should

also be negative then (leaving q_2 out of account). In reality $\frac{1}{2}(\beta_2 - \beta_2^{\,0})\,Q_2$ seems, however, to be about 80 gr. cal., which would point to a comparatively large positive value of Q_2 (hence also to a positive value of Δ_2), but seeing the deviating value of WINKELMANN, little can be said with certainty about this. Indeed, we know little or nothing about the value of $\beta - \beta_0$.

5. <u>$C_2H_5OH - CH_3OH$</u>. Here we have:

p_k	T_k	θb_k	$T_k \cdot id.$	τ	φ	$\sqrt{\varphi}$	λ_1	λ_2
63.0	516.2	8.194	4230	0.8959	0.7929	0.8904	1.113	1.003
78.5	513.1	6.536	3354					

This gives:

$w = \frac{7}{2} \times 1{,}113 \times 513{,}1\,(0{,}01084 +$

$\qquad\qquad + \frac{1}{6}\,1{,}003 \cdot 0{,}1041\,\{0{,}1095^5 - \frac{1}{4}\,1{,}113 \cdot 0{,}1041 \cdot 1{,}7929\})$

$\quad = 1999\,(0{,}01084 + 0{,}01740\,\{0{,}1095^5 - 0{,}0519^8\})$

$\quad = 1999\,(0{,}01084 + 0{,}00100) = 1999 \times 0{,}01184 = \mathbf{23{,}7}$ gr. cal.

The term with Δv would, therefore, in any case be about 9% of the principal term. Further:

$$\Delta v / v = \frac{1}{24}\,1{,}113 \cdot 0{,}1041 \cdot 0{,}0576^2 = \mathbf{0{,}00028}.$$

Accordingly more or less these values would have to be found, when the alcohols were *not* associated. In reality, however $\Delta v / v = 0{,}00004$ is found, which points to a certain volume contraction in both

alcohols. Bose [1]) found about 0,8 for w at 17°,3. This is considerably less than 23,7, so that actually heat is liberated in consequence of the volume contraction.

If *water* is one of the components, the values of Δv and w are generally much greater. Thus e.g. Bose [2]) (w) and Young (Δv) found:

$$a)\ CH_3OH—H_2O \quad | \quad w = -196 \quad | \quad \Delta v/v = -0,030$$
$$b)\ C_2H_5OH—H_2O \quad | \qquad -114 \quad | \qquad\quad -0,026$$
$$c)\ C_3H_7OH—H_2O \quad | \qquad +\ 6 \quad | \qquad\quad -0,030$$

To form again an idea of what actually takes place I have once more calculated the quantities w and Δv according to (10^a) and (11) — which formula is, strictly speaking, only valid for normal components, but can yet in approximation be also applied for the calculation of the *normal* effect also in anomalous components. I have done so for

6 $\underline{C_2H_5OH—H_2O}$. We have then:

p_k	T_k	θb_k	$T_k . id.$	τ	q	$\sqrt{\varphi}$	λ_1	λ_2
63.0	516.2	8.194	4230	0.5382	0.4551	0.6746	1.467	0.8989
217.5	647.1	2.975	1925					

From this is calculated:

$w = \frac{7}{2} \times 1,467 \times 647,1\ (0,2153 +$
$\qquad\qquad + \frac{1}{6}\ 0,8989\ .\ 0,4618\ \{0,3254 - \frac{1}{4}\ 1,467\ .\ 0,4618\ .\ 1,4551\})$
$\quad = 3323\ (0,2153 + 0,06919\ \{0,3254 - 0,2464\})$
$\quad = 3323\ (0,2153 + 0,0055) = 3323 \times 0,2208 = \mathbf{734}$ gr. cal.

For $\Delta v/v$ would be found:

$$\Delta v/v = \frac{1}{24}\ 1,467\ .\ 0,4618\ .\ 0,0790 = \mathbf{0,00223}.$$

And thus $+734$ is reduced to -114, and $+0,0022$ to $-0,0026$. The great volume contraction (for the greater part owing to the water) certainly chiefly determines the strong liberated heat-effect. We shall not enter further into this, and only briefly return to

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[1]) At 21° $0,007 \times \frac{1}{2}(32 + 46) = 0,3$, which reduced to 17°,3 gives 0,8 (see the tables of L. u. B.).

[2]) 50 mol. % $= 64$ weight % gives at a) $-7,77 \times \frac{1}{2}(18 + 32) = -194$ (19°,7) or -196 at 17°,3. Further at 72 weight. % of b) $w = -3,55 \times \frac{1}{2}(18 + 46) = -114$ (17°,3). Winkelmann found the same thing in 1907. And at 77 weight % of c) is $w = +0,50 \times \frac{1}{2}(18 + 60) = +19,5$ (21°) or $+6$ at 17°,3.

the question, why the values of $a/_{v^2}$ will not differ much in many cases, as KATZ thinks he has observed.

10. Some remarks on the values of $a/_{v^2}$.

In the first place it may be stated that in $w = \triangle P + a/_{v^2} \triangle v$, $\triangle P$ is, of course, only negligible when in consequence of great volume contraction in associating components (chiefly water) the term with $a/_{v^2} \triangle v$ greatly preponderates. Only then $w/\triangle v$ may, of course, be put $= a/_{v^2}$ in approximation.

But in the second place $a/_{v^2} = a/_{b^2}$ is not yet always constant within narrow limits. A look at a table[1]) of critical pressures is enough to convince one of this. In water $p_s = 217{,}5$ atm.; in many elements (metals e.g.) still much higher. In many "ordinary" substances, however, especially organic ones), the critical pressures will be about between 30 and 60 atm., as extreme values. And in many only between 40 and 50 atm.

All this is the consequence of the fundamental *atomistic* values of $\sqrt{a}$ and b, from which the values of $\sqrt{a}$ and b *for the molecule can be calculated additatively* in all compounds according to fixed rules (see my papers on this subject already cited in I).

As an example let us take the following principal elements, of which organic substances are built up.

	H	C	N	P	O	S	F	Cl	Br	I
$10^5\, b\; = $	34(14)	100(75)	60(85)	140	70(50)	125	55	110	165	220
$10^2\, \sqrt{a} = $	1.6	3.1	2.9	6.4	2.8	6.3	2.8	5.4	6.9	9
$10^3\, b/\sqrt{a} = $	21(9)	32(24)	21	22	25(18)	20	20	20	24	24

And as the values of $b/\sqrt{a}$ do not differ so very much, this will, of course, not be the case either for the compounds built up of these elements, since — as was already mentioned — the values of b and $\sqrt{a}$ can be additatively calculated from the fundamental values recorded above.

Before concluding I will just draw attention in this connection to the fundamental values of $\sqrt{a}$ in *carbon*. In four single bonds the C-atom is towards the outside quite shaded as regards its attract-

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[1]) Cf. e.g. p. 7 of my first Paper on the additivity cf b and $\sqrt{a}$ in the J. d. Ch. ph. (1916) or These Proc. Vol. XVIII N⁰. 8 p. 1220 et seq.

ive action, by the surrounding atoms or atom groups (Examples CH_4, CCl_4, C_2H_6, CH_3Cl, $CHCl_3$, etc., etc. — cf. also p. 22 J. d. Ch. ph.; also $SnCl_4$, $GeCl_4$, etc.).

In *double bonds*, on the contrary, *part* of the C-atom are left free again, and is $10^2 \sqrt{a} = 1,55$, exactly half[1]) of the normal value 3,1. In triple bonds the *whole* C-atom can exert an attractive action towards the outside, so that then $10^2 \sqrt{a} = 3,1$.

Accordingly in the compound under consideration the value of $10^2 \sqrt{a}$ is 1,55 greater for *every* C-atom with double bond, than corresponding single bond. The *amount of energy e*, which contains the term $- a/v$, will, therefore, be *smaller* by a proportional value. WIBAUT (Ch. Weekblad N°. 24 of 17th June 1922, p. 259) really states that the value of the energy of a double bond is from 10 to 20 cal. smaller than in a single bond. All this finds its explanation in the theory concerning $\sqrt{a}$ and b for all possible kinds of compounds given by me in 1916, which theory has, unfortunately, remained unnoticed by many up to now.

Tavel sur Clarens (Suisse), Sept.—Oct. 1912.

[1]) Thus e. g. in all aromatic compounds, in C_2H_4 etc.; compare the table on p. 20 J. de Ch. ph.

Physics. — "*On* Whittaker's *Quantum mechanism in the atom*". By Prof. H. A. Lorentz.

§ 1. Some months ago Whittaker [1]) has proposed an interesting model by means of which the quantum properties of the atom can be accounted for to a certain extent, the model showing in the first place how it may be that, in the collision of an electron against an atom, the former loses either no energy at all, or just a definite amount of it. In what follows I shall offer some remarks about the action between an atom and an electron, as it would be according to Whittaker's views.

Whittaker supposes that, when an electron approaches an atom, a "magnetic current" is set up in this particle, comparable with the electric current that is excited in a diamagnetic particle by the approach of a magnetic pole. In this latter case the induced current makes the particle repel the pole (Lenz's law) and similarly in the former case the magnetic current gives rise to a force tending to stop the motion of the electron.

The theory takes the simplest form when it is assumed that there are not only "electric charges", but also "magnetic" ones, accumulations of positive or negative magnetism. By the introduction of these into the fundamental equations, the parallelism between the electric and the magnetic quantities can be clearly brought out.

§ 2. Let ϱ be the density of the electric charge, $\mathbf{v}$ the velocity of one of its points, and similarly μ the density of magnetic charge, $\mathbf{w}$ its velocity; further $\mathbf{d}$ the electric force or the dielectric displacement in the aether, and $\mathbf{h}$ the magnetic force or magnetic induction. Then we have the fundamental equations

$$div\ \mathbf{d} = \varrho, \quad \cdots \cdots \cdots \quad (1)$$

$$div\ \mathbf{h} = \mu, \quad \cdots \cdots \cdots \quad (2)$$

$$rot\ \mathbf{h} = \frac{1}{c}(\dot{\mathbf{d}} + \varrho\,\mathbf{v}), \quad \cdots \cdots \cdots \quad (3)$$

$$rot\ \mathbf{d} = -\frac{1}{c}(\dot{\mathbf{h}} + \mu\,\mathbf{w}) \quad \cdots \cdots \cdots \quad (4)$$

[1]) E. T. Whittaker, On the quantum mechanism in the atom, Proc. Royal Society Edinburgh **42** (1922), p. 129.

The force with which the field acts on unit of electric charge is given by

$$f = d + \frac{1}{c} [v . h] \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and there is a corresponding force

$$g = h - \frac{1}{c} [w . d] . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

acting on unit of magnetic charge.

Remarks on the fundamental equations.

1. In order to simplify the mathematical treatment all quantities occurring in the equations are considered as continuous functions of the coordinates.

2. We shall suppose that, while points of an element of volume move with the velocity v varying from point to point, the electric charge of the element remains constant, so that the density ϱ changes in the inverse ratio as the size of the element. We shall make a similar assumption concerning the magnetic charge. By these assumptions the distributions, both of the electric current $\dot{d} + \varrho v$ and of the magnetic current $\dot{h} + \mu w$ are made to be solenoidal, as they must be if equations (3) and (4) shall be true.

3. For the sake of generality we have introduced different symbols v and w for the velocities of the electric and the magnetic charges. These charges may be imagined as penetrating each other and having independent motions.

§ 3. The fundamental equations form a consistent system and are in good agreement with ideas and theorems which physicists would be very unwilling to give up.

The force acting on the electric and the magnetic charges contained in an element of volume, taken per unit of volume, is given by

$$\varrho f + \mu g = \varrho d + \mu h + \frac{1}{c} [\varrho v . h] - \frac{1}{c} [\mu w . d]$$

and for the x-component of this force one finds after some transformations

$$\varrho f_x + \mu g_x = \frac{\partial X_x}{\partial x} + \frac{\partial X_y}{\partial y} + \frac{\partial X_z}{\partial z} - \frac{\partial G_x}{\partial t}$$

where

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$$X_x = \tfrac{1}{2}(d_x{}^2 - d_y{}^2 - d_z{}^2) + \tfrac{1}{2}(h_x{}^2 - h_y{}^2 - h_z{}^2),$$

$$X_y = d_x\,d_y + h_x\,h_y, \qquad X_z = d_x\,d_z + h_x\,h_z, \text{ etc.,}$$

$$\mathbf{G} = \frac{1}{c}\,[\mathbf{d}\,.\,\mathbf{h}].$$

This shows that the ponderomotive forces can still be expressed by means of MAXWELL's stresses and of the electromagnetic momentum **G**. It should be noticed that this is possible because we have the positive sign in (5) and the negative sign in (6).

The well known expressions for the electric and the magnetic energy and for the flow of energy likewise remain unchanged. Indeed, starting from the fundamental equations, one finds for the work, per unit of time and unit of volume, of the forces exerted by the field

$$(\varrho\,\mathbf{f}\,.\,\mathbf{v}) + (\mu\,\mathbf{g}\,.\,\mathbf{w}) = -\frac{\partial E}{\partial t} - \operatorname{div}\mathbf{S},$$

$$E = \tfrac{1}{2}(\mathbf{d}^2 + \mathbf{h}^2), \qquad \mathbf{S} = c\,[\mathbf{d}\,.\,\mathbf{h}].$$

§ 4. If the distribution and the motion of the charges are known, the field can be calculated by means of two scalar potentials φ,χ and two vector potentials **a, b**. These functions are given by the formulae

$$\varphi = \frac{1}{4\pi}\int\frac{[\varrho]}{r}\,dS, \qquad \chi = \frac{1}{4\pi}\int\frac{[\mu]}{r}\,dS,$$

$$\mathbf{a} = \frac{1}{4\pi c}\int\frac{[\varrho\,\mathbf{v}]}{r}\,dS, \qquad \mathbf{b} = \frac{1}{4\pi c}\int\frac{[\mu\,\mathbf{w}]}{r}\,dS,$$

in which the integrations have to be extended over all space. The distance from the point for which one wants to determine the potentials for the time t is denoted by r and the meaning of the square brackets is that the quantities ϱ, etc. have to be taken such as they are at the time $t - \dfrac{r}{c}$.

In terms of the potentials we have for the field

$$\mathbf{d} = -\frac{1}{c}\,\dot{\mathbf{a}} - \operatorname{grad}\varphi - \operatorname{rot}\mathbf{b},$$

$$\mathbf{h} = -\frac{1}{c}\,\dot{\mathbf{b}} - \operatorname{grad}\chi + \operatorname{rot}\mathbf{a}.$$

§ 5. We shall now suppose, following WHITTAKER, that in the atom there is a circular ring R, over which magnetism is uniformly distributed. We shall consider it as very thin, so that we may speak

of a "line", and we shall denote by a the radius and by k the amount of magnetism per unit of length. Let the centre O be taken as origin of coordinates, the axes OY and OZ being in the plane of the circle, and let s be the distance from a fixed point, measured along the circle. The positive direction of s will be determined by the rotation $OY \rightarrow OZ$, and will therefore correspond, as we shall say, to the direction of OX. We shall finally suppose the ring to be a rigid body that can only rotate about OX, and we shall in the first place calculate the couple acting on it when an electron with charge e moves in the neighbourhood.

The force on an element ds is $k\mathbf{g}\,ds$ and its moment with respect to OX $ak\mathbf{g}_s\,ds = ak\mathbf{h}_s\,ds$. Thus the resultant couple is $ak\int \mathbf{h}_s\,ds$, where the value of the integral may be deduced from (3). For this purpose we imagine some stationary surface σ having the circle R for its boundary and the normal n to which is drawn in a direction corresponding to the positive direction of s. Then, if this surface does not intersect the electron,

$$\int \mathbf{h}_s\,ds = \frac{1}{c}\int \dot{\mathbf{d}}_n\,d\sigma = \frac{1}{c}\frac{d}{dt}\int \mathbf{d}_n\,d\sigma \quad . \quad . \quad . \quad . \quad (7)$$

We shall suppose the motion of the electron to be so slow and to change so slowly that it may be said, in any of its positions P, to be surrounded by the electric field that would exist if the electron were at rest in that position. Then the last integral in (7) has the value $\frac{e}{4\pi}\omega$, if ω is the solid angle subtended at P by the ring R, the sign of ω depending on the direction, towards the positive or the negative side, in which straight lines drawn from P pass through the surface. Hence, the equation of motion of the ring will be (ϑ angular velocity, Q moment of inertia)

$$Q\frac{d\vartheta}{dt} = \frac{ake}{4\pi c}\frac{d\omega}{dt} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

If this equation is to hold for a certain lapse of time, the surface σ must be chosen in such a way as not to be traversed by the electron during that interval.

Now, two cases must be distinguished, the electron passing or not passing across the circular plane within the ring, or, as we shall say, through the ring. In the latter case, σ may be made to coincide with the circular plane and we shall have, both before and after the encounter, if the electron is at a great distance,

$\omega = 0$. In the former case this will not be true. Let us suppose that the electron goes through the ring once, in the positive direction, and let A and B be two positions, before and after the encounter, both far away from the ring. Then, whatever be these positions, provided only that they do not coincide, we can choose the surface σ in such a way that it is not intersected by the path of the particle from A to B, and that $\omega = 0$ at the point A. It is easily seen that then the final value will be $\omega = 4\pi$.

Bij integration of (8) one finds

$$\vartheta = \vartheta_0 + \frac{a k e}{4 \pi c Q}\, \omega, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

if ϑ_0 is the angular velocity which the ring may have had before the encounter.

§ 6. We have next to consider the motion of the electron. The rotation of the ring constitutes a magnetic current

$$i = a k \vartheta \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

giving rise to an electric field that is easily determined if we suppose it not to differ appreciably from the field that would exist if i were constant. The calculation, exactly similar to that of the magnetic field due to an electric current (the vector potential **b** is first determined and then **d** = — rot **b**) leads to the result

$$\mathbf{d}_x = - \frac{i}{4 \pi c}\frac{\partial \omega}{\partial x}, \quad \mathbf{d}_y = - \frac{i}{4 \pi c}\frac{\partial \omega}{\partial y}, \quad \mathbf{d}_z = - \frac{i}{4 \pi c}\frac{\partial \omega}{\partial z}, \quad . \quad (11)$$

from which, combined with (10) and (9), we can deduce that the force $e\,\mathbf{d}$ acting on the electron depends on a potential

$$\psi = \frac{a k e}{4 \pi c}\, \vartheta_0\, \omega + \frac{a^2 k^2 e^2}{32\, \pi^2\, c^2\, Q}\, \omega^2 \quad . \quad . \quad . \quad . \quad (12)$$

If we wanted exactly to determine the motion we should also have to take into account the force with which, owing to its velocity, the electron is acted on by the magnetic field that is due to the ring and to stationary magnetic charges eventually existing in the atom, and so the problem would become very difficult. Since, however, the latter force does no work, we can write down the equation of energy

$$\tfrac{1}{2}\, m\, v^2 = \tfrac{1}{2}\, m\, v_0^2 - \psi, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

(v_0 the initial velocity at a point where $\omega = 0$) and this is sufficient for some interesting conclusions.

Indeed, if the electron has not passed through the ring, we shall have finally $\omega = 0$, $\psi = 0$, so that at the end of the encounter the angular velocity of the ring and the velocity of the electron will again have their initial values ϑ_0, v_0. This will also be the case if the electron goes twice through the ring, first in the positive and then in the negative direction.

If, however, it goes through the ring no more than once, the final value of ω will be 4π and according to (12) and (13) the electron will have lost an amount of energy

$$\frac{a k e}{c}\vartheta_0 + \frac{a^2 k^2 e^2}{2 c^2 Q}.$$

The ring will have gained just as much. This follows directly from (9) and also from the remark that, as may be seen by (9) and (13),

$$\tfrac{1}{2} m v^2 + \tfrac{1}{2} Q \vartheta^2$$

remains constant during the motion.

In the case $\vartheta_0 = 0$ the energy that is imparted to the ring by an "effective" encounter is given by

$$\frac{a^2 k^2 e^2}{2 c^2 Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

This agrees with WHITTAKER's result. In his calculations he has confined himself to a motion of the electron along the axis of the ring, but the preceding considerations show that the theory can easily be generalized. However, it is also seen that, if in an effective encounter the ring is to receive the amount of energy represented by (14), the rotation which may have been imparted to it by a previous encounter, must first have disappeared in one way or another.

§ 7. If, in the case $\vartheta_0 = 0$, the electron is to pass through the ring for good and all, it must initially have at least the amount of energy (14). If it has less, it can by no means get beyond a point, where

$$\psi = \tfrac{1}{2} m v_0^2 \quad , \quad \omega = \frac{4 \pi c v_0}{a k e} \sqrt{m Q} \quad . \quad . \quad . \quad . \quad (15)$$

Such a point is really reached, the electron returning after having got to it, when the motion is along the axis. In general, however, the problem is less simple. The locus of the points which satisfy the condition (15) is a surface limited by the circle R and having, for a somewhat high value of v_0, the shape of a wide bag lying on the positive side of the circle, which forms its opening. An

electron that flies into this bag can never leave it across the surface which it will perhaps not reach at all. Indeed, it may be that, before the velocity is exhausted, its direction comes to be tangential to a surface $\omega = $ const., characterized by a value of ω smaller than the one given by (15). It seems probable that in such a case the electron, after having moved in the bag for a certain length of time, will leave it through the opening, but it is difficult to make sure of this. [1]

§ 8. In WHITTAKER's model the ring R is made up of the poles, of equal signs, of a number of magnets arranged along radii of the circle and having their opposite poles at or near the centre. It might seem at first sight that in a structure of this kind the magnets can be replaced by perfectly conducting solenoids carrying pre-existent electric currents, so that we can do without magnetic charges.

In reality, however, no satisfactory model can be obtained in this way. This is seen most easily when the electron is supposed to move along the axis $O\,X$. In the magnetic field due to this motion the lines of force are circles around the axis, and therefore the force acting on an element of current at a point P, is directed along a line lying in the plane $P\,O\,X$. For such a force the moment with respect to $O\,X$ is zero; consequently, neither a solenoid nor a system of solenoids can be acted on by a couple tending to produce a rotation about $O\,X$.

Thus it would seem that the hypothesis of "magnetism" existing independently of electric currents is quite essential in WHITTAKER's model. I need not speak at length of the reasons for which such an assumption is not to be readily admitted. Let it be remarked only that the equations (1)—(6), though forming a consistent system, do not allow us to establish variation theorems of the kind of HAMILTON's principle. In this principle we are concerned with the *difference* between the potential and the kinetic energy, so that, in the equations, the two energies do not occur in the same way. Now, if there are only electric charges, we can, as is well known, arrive at an equation of the Hamiltonian form, in which $\frac{1}{2}\mathbf{d}^2$ takes the place of the potential and $\frac{1}{2}\mathbf{h}^2$ that of the kinetic energy. If there are only magnetic charges, there is a similar formula, in which, however, the electric

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[1] An interesting discussion of this question has been given (Phil. Mag. **44**, 1922, p. 777) by Mr. B. B. BAKER, wo has considered the case of an electron not moving along the axis of the ring, without, however, taking into account the forces that may arise from the existence of a magnetic field.

and the magnetic energy have changed their parts. It is clear that it must be difficult to combine the two theorems into one.

I must not omit to say that WHITTAKER does not want to attach too great importance to the special form of his model. He aptly remarks that, after having obtained a satisfactory system of equations, we may discard the model by which we have been led to it. What is especially interesting in WHITTAKER's idea seems to me to be this, that it shows the possibility of a sharp criterion by means of which it can be decided whether an encounter is effective or otherwise. Such a criterion there must certainly be.

§ 9. Generalization of the model. Suppose that there is in the atom a definite closed circuit s, in which a magnetic current i may circulate, the energy being $\frac{1}{2} L i^2$. Then we have the differential equation

$$L \frac{di}{dt} = \int \mathsf{h}_s \, ds,$$

or, if an electron moves near the atom,

$$L \frac{di}{dt} = \frac{e}{4\pi c} \frac{d\omega}{dt}.$$

Take this instead of (8), and combine it with (11). The amount of energy that is transmitted in an effective encounter (initially $i = 0$) is now found to be

$$\frac{e^2}{2c^2 L} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

In order to obtain a "vibrator" [1]) we can link the circuit s with another circuit s', in which an electric current can circulate (no resistance, energy $\frac{1}{2} L' i'^2$); indeed, we have

$$L \frac{di}{dt} = \frac{1}{c} i' \qquad , \qquad L' \frac{di'}{dt} = -\frac{1}{c} i.$$

The frequency is given by

$$v = \frac{1}{2\pi c \sqrt{L L'}}.$$

If now an electron passes through the circuit s in a time that is short in comparison with the period, the vibrator receives the amount of energy (16) and this amount will subsequently be radiated. It will be equal to hv if

$$\frac{\pi e^2}{c} \sqrt{\frac{L'}{L}} = h.$$

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1) Cf. WHITTAKER, l.c. § 5, p. 139.

One can also try to illustrate other phenomena by means of the model. In its passage from one stationary state of motion to another an electron may be imagined to go through the circuit s of a vibrator, so that the energy which it loses is first imparted to the vibrator and then radiated by it. Conversely, after having taken in some way from a beam of incident light the energy $h\nu$, the vibrator could give this energy to an electron that passes through it at the right moment. But in all this we are confronted with very serious difficulties.

Psychiatry. — *"Concordance of the Laws of some Psychological and Physiological Phenomena"*. By Prof. E. D. WIERSMA.

The phenomena of consciousness are attended with material changes in the brain. There is an uninterrupted continuity in the anatomic as well as in the psychic phenomena. The two groups of phenomena run parallel. A change in the one will be accompanied by a change in the other. Whether we consider the phenomena of consciousness from the psychological or the physiological standpoint, in both cases the result will be the same, because the changes in the one differ from those in the other not intrinsically but only in form. Memory, which we conceive to be the retention and reproduction of previous impressions, has been considered physiologically and psychologically. First ARISTOTLE and afterwards HERING have looked upon it as a general function of the organised matter. SEMON, who has written a pre-eminent monograph on the Mneme, deemed the ordinary terminology inadequate, as it concerned chiefly the phenomena of consciousness. He, therefore, introduces other terms, as engrams, i.e. the organic changes evoked by a stimulus; the retention of those impressions, which afterwards may again come to us as consciousnesses, is the mneme; and the stimuli by which the action of the primary stimulus can be re-aroused, are termed ekphoric stimuli. Under certain conditions permanent connections are formed between the several engrams, which have been termed "regular tracks". By the side of this anatomical interpretation the psychological explanation may be put forward. We know for certain that every impression leaves an after-effect in consciousness. Mental tests on secondary function, psycho-analysis, the symptoms of hysteria, hypnosis have conclusively established the existence of these after-effects. That these after-effects may become consciousnesses again through association, is borne out by self-observation and by experiment. Thus the psychological conception may be formed directly, whereas for the physiological we have first to pre-suppose all sorts of organic changes, for we are still completely ignorant of the real existence of the organic engrams and the regular tracks. In strictness this

interpretation is physïological only on the outside; at bottom it is psychological.

Emotions reveal themselves in two ways: Self-observation tells us what emotion in reality is, and from the expression of emotions we deduce what the feelings of the affected individual really are. We know that these peripheral phenomena play so important a rôle that some regard the expression of an emotion in reality as the source of emotion, as a conscious progress. Many psychologists still adhere to this "JAMES-LANGE-theory". However, LEHMANN has shown by dint of many arguments that emotion is primary and expressional movement is secondary. One of his arguments is that the change in the blood-supply, in respiration etc., is posterior to the real emotion. The experiment upon which this argument is based, is open to objection, as it is often difficult to make out where exactly the change in the plethysmogram or the breathing begins. This induced me to repeat the experiment registering at the same time the psychogalvanic reaction. In comparing the plethysmogram with the psycho-galvanogram the latter appears to be more reliable, as is borne out by the subjoined curves.

Respiration
Galvanogram
Plethysmogram
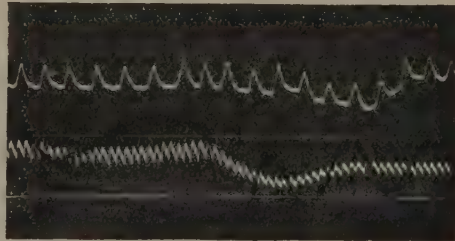
The beginning of the reaction is clearly marked, whereas in the plethysmogram it is often doubtful with which pulsebeat the reaction really begins. The subjoined table also clearly indicates that the

Physiological reactiontimes to pain-sensations
in $^1/_{100}$ sec.

Galvanogram	Plethysmogram
220	335
230	360
210	280
210	350

reaction-times of the psycho-galvanogram are shorter and much more constant.

These physiological reactions times, of which I mention only a few, are considerably longer than the psychological reaction times to pain-stimuli which occur directly after the touch-stimuli.

Thus, although emotion i.e. the psychical, is to be considered as primary, it is nevertheless a fact that the expressional movements largely influence the nature and the intensity of emotion. Intense emotions become less vivid through strong expressional movements.

Having a good cry and screaming lessens our grief, hysteric affective conditions, which accompany weeping and screaming are of short duration, the raptus melancholicus has soon spent itself. Here we have to do with an inhibitory process of two co-existing complexes of consciousness. The experience of the violent expressional movements inhibits the emotion.

This accounts for the custom among some uncivilised peoples of dissipating grief by selfmutilation. Not only involuntary but also voluntary expressional movements inhibit emotion. The intensity of a sad mood is often lessened by assuming the attitude and the countenance of cheerfulness.

So far we have seen that conscious as well as unconscious will-acts bear upon emotion in the same way. Conversely, we will now discuss the way in which emotion affects the will-acts.

Emotions exert a great influence upon other complexes of consciousness. They largely inhibit them, because attention clings to them tenaciously. Regular thinking is impossible. Voluntary movements are also inhibited. We don't get on with our work, all our activities slacken, and in pathological cases, such as melancholy, a complete relapse may ultimately set in. Again, this does not apply to voluntary movements only. Also the unconscious efferent impulses are subject to the same influence. Cannon [1]) showed that in cats, in a state of emotion, the food remained in the stomach longer than in that of normal cats. Similar inhibitory processes occur in man. A melancholiac secretes less saliva and fewer tears. This can be established experimentally.

Furthermore a distinct decrease of motility of the stomach and the intestine is demonstrable in man. When administering 0,1 I. K. in the empty stomach according to Sahli's [2]) prescription, iodine will be found in the urine and in the saliva under normal conditions after 15 minutes. According to Sahli I. K. is not resorbed

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[1]) Cannon: Bodily Changes in Pain, Hunger, Fear and Rage. 1918.

[2]) Sahli: Klinische Untersuchungsmethoden I, p. 564 u. p. 568.

at all in the stomach, or only after a long interval, so that with a decreased motility of the stomach the I-reaction in urine and saliva will appear later than in normal cases. This experiment was performed with some melancholiacs and with some normal persons:

Iodine-reaction in urine				Iodine reaction in saliva			
Melancholy		Normal		Melancholy		Normal	
A	105 min.	K	15 min.	A	— min.	K	15 min.
B	105 „	L	15 „	B	165 „	L	45 „
C	90 „	M	15 „	C	90 „	M	·15 „
D	60 „	N	15 „	D	— „	N	15 ,
E	75 „	O	15 „	E	90 „	O	15 „
F	75 „			F	45 „		
G	45 „			G	90 „		
H	60 „			H	60 „		
I	45 „			I	45 „		

This table shows distinctly the retardation of the reaction in urine and saliva in cases of melancholy. It is very well possible that this retardation is not due only to the gastric function, but that at the same time a slower resorption has taken place in the intestine and inhibition in the secretion of the kidneys and the salivary glands.

Conclusive evidence regarding the retardation of the movement of the stomach and the intestine can be afforded by Röntgenograms.

In the morning 150 grs of bariumsulphate was administered with 500 grs of porridge in the empty stomach. Normally the stomach will then be quite empty again after 4—6 hours. In the stomach of a melancholiac I found after 4 hours still a very large quantity; after 10 hours a rather large quantum and after 24 hours still distinct traces of the bariumsulphate. After a 10 hours' fast this patient took food again, so that the bariumsulphate, then present, may have been mixed up with the food. The latter registration, therefore, is not quite reliable.

The decreased motility of the intestine also manifests itself distinctly. Under normal conditions all the bariumsulphate is removed from the small intestine after 10 hours. The examination of another

melancholiac proved clearly that after this lapse of time still considerable amounts are present.

In the same way slower motility of the large intestine can also be established. In one patient the food remained in the large intestine for 4 days, in others for more than 5 days.

It is evident that relative to the emotions the conscious will-acts and the unconscious centrifugal impulses are subject to the same rules.

In discussing the reflexes it appeared that mutual inhibition of co-existing phenomena of consciousness also applies to simultaneous unconscious centrifugal impulses. BABINSKI's reflex is superseded by the normal plantar reflex, the sucking- and the gait-reflex by other movements, arising later, the diminution of the patellar reflex is the result of centrifugal impulses that are always present, the tonus of the antagonists diminishes through contraction of the agonists. All this proves that the co-incidence of involuntary efferent impulses gives rise to a mutual inhibition in precisely the same way as with the co-incidence of conscious will-acts. Hereby a complete co-operation of the muscles is rendered possible.

Closely related to this are the associated movements. When a child begins to grasp at things with the right hand, the left one accompanies it. A few years later these "co-operations" disappear. They are inhibited. Whence does this inhibition arise? An incessant flux of impressions passes from the extremities to the area of consciousness, imparting information regarding attitude and position of the limbs, so that the easiest attitude will be selected and every undesired movement will be counteracted. At first this occurs arbitrarily, afterwards involuntarily and reflexly. A gymnast and a skater will first try to counteract the unnecessary movements, afterwards this happens involuntarily. That the inhibitory action is exerted by these simultaneous centrifugal reflex impulses may be gathered from the following facts:

Associated movements are strongest in the first years of life. When the position reflexes begin to develop, the associated movements will gradually cease.

They will recur or intensify in highly emotional situations. The pre-occupation resulting from them will not only eliminate all complexes of the central area of consciousness, but also the subliminal position-reflexes will be affected by them, so that the associated movements of a deeper level will recur. In the same way in con-

ditions of dementia, as with dementia paralytica and dementia senilis, in which a general diminution occurs of the degree of consciousness, the position-reflexes are affected prior to the associated movements. It is obvious, therefore, that the associated movements will recur.

Associated movements manifest themselves most distinctly with an affection of the pyramidal tract, because then the conduction of the centrifugal impulse, which acts inhibitively, is lacking. This is easy to demonstrate in patients with cerebral hemiplegia, because in these cases the associated movement of the paretic leg can be directly compared with the movement of the healthy leg. In my investigation I availed myself of the following associated movement. When a subject, in dorsal position, is instructed to raise the right leg, the left leg will be pressed down, of which fact the experimenter may readily convince himself by putting his hand under the left heel. A distinct pressure will then be perceived, which will increase with a greater effort of the right leg. The associated movement of the left leg may be reinforced by opposing a resistance to the movement of the right leg. The registration of the associated movement happens in the following way. The left leg is suspended in a loop a little way above the heel. The loop is attached to a steel-yard by means of a cord that passes over a pulley. When the leg is pressed down the force of the effort can be read accurately from the steel-yard. To the cord is fastened a stylus, which records the movement directly on a rotating kymograph. In patients with cerebral hemiplegia the associated movement on the paretic side appears to be much more pronounced than on the healthy side. In the subjoined curves A', A" and A''' represent the associated movements of the normal leg;

A' Associated movement of the normal leg.
B' Associated movement of the paretic leg.

I.

A" Associated movement of the normal leg.
B" Associated movement of the paretic leg.

II.

A''' Associated movement of the normal leg.
B''' Associated movement of the paretic leg.

III.
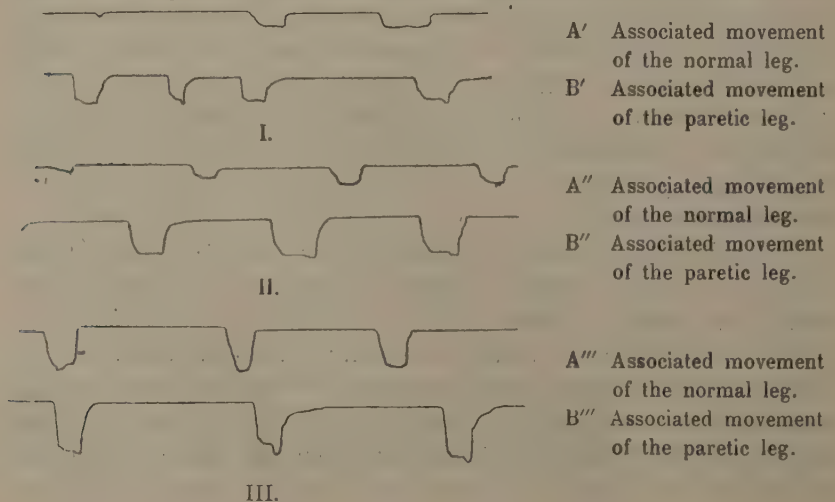
B', B'' and B''' those of the paretic leg. In curve I the associated movement is registered without any impediment to the other leg. In curve II the leg is weighted with 1700 grms, and in curve III with 2900 grms.

The annexed table also shows clearly that the associated movement of the normal side is invariably inferior to the one on the paretic side.

Curve I		Curve II		Curve III	
normal leg	paretic leg	normal leg	paretic leg	normal leg	paretic leg
gr.	gr.	gr.	gr.	gr.	gr.
162	767	225	975	1247	1175
490	767	427	873	1302	1201
438	751	592	876	1064	1453

Associated movements are on a par with the associations of the phenomena of consciousness. As known, the laws under which these associations originate have been reduced to the simultaneous associations. That this is also the case with the asssociated movements is evident. The child begins to stretch both hands when grasping at something, which evolves a simultaneous association. When, in later years the grasping right hand is accompanied by a movement of the left one, this is in reality an association effected in precisely the same way, in which e.g. the image of a person is called up when hearing his name.

Associations can be facilitated or inhibited. In this also the associated movements bear so close a resemblance to associations, that the two processes must be considered analogous.

Associations are inter alia facilitated by greater intensity of the associated ideas. EBBINGHAUS introduced meaningless syllables to be learned by heart in a certain order. Reproduction in a reversed order was not possible. Of this MÜNSTERBERG has put forward an explanation: In reciting the alphabet, a and b remain for some time in consciousness. In hearing b there is still a faint after-effect of a. Therefore, in hearing a, b will be reproduced sooner than, conversely, a will be reproduced in hearing b. In the associated move-

ments the same phenomenon manifests itself. The intensest associated movements persist longest. They display a much greater resistance to the inhibiton. There are people with whom some associated movements persist through life e.g. the mouth-movements when they are using scissors.

Associations are also promoted by the intensity of the associating idea. Memory-images will be reproduced the more readily according as the associating idea is more intense and distinct. Experience e.g. teaches us that visual, and auditory sensations arouse associations sooner and more distinctly than the vague olfactory, and gustatory sensations. We can observe a similar phenomenon in the associated movements. The curves obtained from the above experiments go to show that, when the movement of the one leg is interfered with by a weight thus inciting the subject to greater exertion, the associated movements of the other leg also increases.

In curve II the weighting of both the paretic, and the normal leg considerably increased the associated movements on either side. When, as in curve III the weight is very heavy, the demand upon the paretic leg is so great, that the ensuing associated movement of the normal leg does not differ much from that of the paretic leg. Curves I and II also demonstrate that, with a series of movements of the paretic leg the associated movements of the normal leg increase in magnitude. This is due to a greater demand upon the paretic leg consequent on fatigue.

The associations of the phenomena of consciousness can also be inhibited. Here again the associated movements exhibit analogous phenomena. As known, the association of the phenomena of consciousness is interfered with by co-existing complexes of consciousness and the degree of the interference depends on their homogeneity. The reproduction of visual ideas is counterected by other sight-experiences in a higher degree than e.g. by auditory experiences. In forming a visual image of a situation, we shut our eyes. Speaking a foreign language is more difficult than to read it, because the word in our native tongue arouses many associations which act inhibitively, whereas the foreign word awakens no other associations than those called up by the native word. It is just the same with the associated movements. The impulses exciting them, are ousted already by the co-existing efferent impulses of the position reflexes. It is evident, that also here there is an analogy to the inhibition exerted upon sight-associations by other visual impressions, and to the inhibition, exerted by the multitude of associations, upon our efforts to speak a foreign language.

The so-called mediate associations occur, when memory-images flash into consciousness that seem to have no connection with the associating idea. On closer inspection it will appear that the associated idea has not linked itself directly to the associating idea, but to an unconscious memory-image. Without this intermediary the association would not have originated. The strange freaks of normal men, of hystericae and in cases of dementia praecox, may often be assigned to these intermediary ideas unsuspected at the moment of the association. Afterwards they crop up again by concentrating ourselves entirely upon the association, or by other means, such as association experiments, hypnosis, etc. Similar phenomena occur in physiological processes. Many renal diseases are attended with hypertrophy of the heart. The real relation is still a moot point; probably the enlargement of the heart arises from the increase of the blood-pressure, which some believe to result again from the retention of the intermediary products of metabolism, or, according to others, from an excess of adrenalin-products. It is evident, then, that here also we have to do with two phenomena mediately connected. A similar example is afforded by hypertrophy of the uterus in pregnancy. This is not a direct action of the foetus upon the uterus, as this hypertrophy also reveals itself in extra-uterine pregnancy. Now, inquiries have proved that most probably internal secretion of the corpus luteum comes into play here. So, here again we observe a connection between the two phenomena through the mediation of one that has long remained unsuspected. The hypertrophy of the mammary tissue in pregnancy is assignable to the same cause.

We have already referred to the phenomena of ousting the centrifugal impulses by conscious will-manifestations and even by other reflex-impulses, nearer to the threshold of consciousness. Definite proof of it is afforded by the superseded reflexes, as that of BABINSKI and the sucking reflex, and the superseded associated movements. As stated above, these reflexes have not disappeared; they recur when the inhibitory influences do not exist any more. In this respect they resemble retrograde amnesia. Here also memory images are stamped out by intensely operating, often highly emotional, impressions. The memories closest to the threshold of consciousness, still exerting their after-effect upon the centre of consciousness (which proves them to be still coexistent with the superseding stimulus), are thrown back farthest from the view-point. We may, then, put it in this way that HEYMANS's ingenious idea is applicable to the superseded reflexes as well as to the superseded thoughts, viz.

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that their distance-energy is enlarged and their level-energy has
decreased.

It seems to me that there is another resemblance of some signi-
ficance. Perceptions, as we observed, do not fade out altogether,
they leave traces, which will be present in consciousness again
through association, but which, of themselves, also possess a tendency,
a certain potency to emerge. There is a continual competition among
the subconscious tendencies. Their potency varies with various
conditions inter alia of novelty, emotionality, fortuitous associations.
In ordinary circumstances there is an uninterrupted inhibition exerted
by other ideas. When this inhibition is taken away, as is the case
in dozing and during sleep, these subconscious ideas may be present
in consciousness again. This may be brought about by association,
but surely their own energy may also co-operate. This appears from
the difference in own energy appropriate to various ideas. For
example: a personal name may recall the image of the person, but
the latter does not always call up the name. An accident will be
reproduced more readily when witnessed than when only read
about. That own energy of ideas or perceptions to become central
consciousnesses, which energy has been termed by HEYMANS distance-
energy, is utilized partly by obviating resistances and, when at the
ingress into consciousness some energy is still left, this remainder
is spent entirely in repulsing the resisting complexes of consciousness
as far as possible into unconsciousness. These conditions occur with
the just-mentioned retrograde amnesia, analogous phenomena of
which are met with in the repulse of some reflexes by others, which
lie still nearer to the threshold of consciousness. But HEYMANS also
puts the case that there are hardly any resistances, so that there
cannot be any question about a loss of distance-energy through
repulse. In such a case that energy will be applied in consciousness
as energy of association, of sentiment, of thought and of will. Now,
do similar manifestations also arise with subconscious phenomena?
As regards some reflex manifestations, we are in a position to select
such conditions as are perfectly similar to those required for the
phenomena of consciousness, so that when they occur there will be
no resistances in their way. In this connection we may take it for
granted, that knee-jerks are inhibited by simultaneous centrifugal
cerebral impulses. Affections of the pyramidal tract have disturbed
the conduction of these impulses, so that the knee-jerks are no longer
subject to inhibition. Well then, in these conditions many reflex-
associations occur, viz. contraction of the adductors, and also frequently
of the m. quadriceps of the other leg.

I annex a few other examples, the number of which may still be enlarged.

It is known that the direction of voluntary thinking and acting is determined by the intentional idea in its after-effect. The bias of the mind arouses the most serviceable thoughts and motives; the others are inhibited. This is the course of every process of thought as well when we are simply designing a travelling plan, as when we are working out the most intricate scientific problem. The same holds also for mental development at large. From our earliest youth upwards there is an unconscious tendency by which the adult mind is developed from the simplest data. Physiologically we observe the same process, by which a single ovum develops into the full-grown body. In either case there is a tendency in the line determined by the result to be attained, i.e. the intentional idea.

True, this result is not present in consciousness, but for the rest it is perfectly similar to the intentional idea in its secondary function, because either of them determines the developing process.

In mental growth the innate tendency dictates a certain trend. Great disparities present themselves, e.g. in the types of observation and in individual character. Interest, which is chiefly innate, plays a prominent rôle in the formation of the types of observation. The visual type e.g. shows an affinity for sight-impressions, while it neglects the auditive-, and the motor impressions. In physical development we distinguish a similar difference in trend. The fertilized ovum cell is omnipotent. In it is hidden the power for development of all tissues. Differentiation of this potency appears after repeated division of the cell. Some cells can supply only epithelium, others only connective tissue, or muscular and bony tissue.

From the facts above stated it appears that there is a far-reaching concordance between the laws of some psychological, and, let me put it cautiously, *some* physiological phenomena. Our results justify us in suspecting that with a fuller knowledge of both groups of phenomena a psychological equivalent may be found for every physiological phenomenon.

Physics. *"On the Separation of Gas Mixtures by Diffusion in a Flowing Gas"*. By Dr. G. HERTZ. (Communicated by Prof. P. EHRENFEST.)

As is well known, the differential equation: $\Delta \varrho = 0$, in which ϱ represents the density of the diffusing gas, is valid for stationary phenomena of diffusion in media at rest. This equation does not contain the constant of diffusion of the diffusing gas at all. If, therefore, the diffusion of a gas mixture is considered, the ratio of the partial pressures of the components of the mixture is constant throughout the space, i.e. unmixing does not occur with such a stationary diffusion phenomenon. This however, is different, as will be shown in what follows, with stationary phenomena of diffusion in a moving medium. As such a moving medium we take a flowing gas. Let the velocity of this gas medium be v, and let it satisfy the condition $div\, v = 0$. The constant of diffusion of the diffusing gas under definite circumstances be δ, its density ϱ, which for the calculation we shall assume to be small compared with the density of the gas medium. The quantity of the diffusing gas passing through the unit surface in the unit of time hence its current density, is equal to the sum of the diffusion and the convection current; it is:

$$i = - \delta\, grad\, \varrho + \varrho\, v$$

For stationary phenomena $div\, i = 0$, so that taking into account that $div\, v = 0$, we get the following differential equation for such phenomena:

$$\Delta \varrho = \frac{1}{\delta}\, (v,\, grad\, \varrho)$$

In contrast with the equation $\Delta \varrho = 0$ holding for a medium at rest, this equation contains the constant of diffusion δ. Accordingly the distribution of the density in space is here dependent upon the constant of diffusion. If, therefore, a gas mixture is made to diffuse in a stationary medium the ratio of the partial pressures is constant. On the other hand this ratio is variable in a moving medium; and this brings about the possibility to use this phenomenon for the separation of gas mixtures.

In what follows two special cases will be treated, which it has been possible to realize experimentally, and which can be used for the separation of gas mixtures. In both cases a gas medium flowing with a constant velocity v is used, the direction of which will be chosen as direction of the negative x-axis. For this case the differential equation is:

$$\Delta \varrho = - \frac{v}{\delta} \frac{\partial \varrho}{\partial x} \ ^1)$$

When we assume $\varrho = \varrho_0$ for $x = 0$, and $\varrho = 0$ for $x = \infty$, we get as a first example the case of diffusion *against* the gas current. The solution is easily seen to be:

$$\varrho = \varrho_0 \, e^{-\frac{vx}{\delta}}$$

The density of the gas diffusing against the current decreases, therefore, according to an exponential function, the gradient of which depends on the ratio of the current velocity to the diffusion constant. When now a mixture of two gases whose partial pressures for $x = 0$ are ϱ_0 resp. ϱ'_0 diffuses against the current, the following equation is found for the ratio of their partial pressures as function of the place:

$$\frac{\varrho}{\varrho'} = \frac{\varrho_0}{\varrho'_0} \, e^{-vx\left(\frac{1}{\delta} - \frac{1}{\delta'}\right)}$$

This distribution agrees in form with the distribution of the partial pressures in the field of gravitation determined by the barometer formula, with the exception only that here the quantity $\frac{v}{\delta}$ takes the place of the specific gravity, and the whole pressure gradient can be brought about at a distance of the order of a millimeter.

If this phenomenon is to be used for the separation of a mixture, the gas present at a certain place, e.g. at $x = l$, must be pumped off. The limiting conditions then become $\varrho = \varrho_0$ for $x = 0$ and $\varrho = 0$ for $x = l$. The solution then becomes:

$$\varrho = C \left(e^{-\frac{vx}{\delta}} - e^{-\frac{vl}{\delta}} \right)$$

in which C is a constant. If, as in practice, $e^{-\frac{vl}{\delta}}$ is small compared with 1, C is approximatiely equal to ϱ_0. We thus find for the

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^{1}) Compare S. Holst Weber, Handelingen van het 17e Nederlandsch Natuur-en Geneeskundig Congres, Leiden 1919.

current density of the diffusing gas, i.e. the quantity which diffuses per unit of time through the unit of crosssection against the current:

$$i = v \, \varrho_{0} \, e^{-\frac{vl}{\delta}}$$

If a mixture of two gases which at $x = 0$ have the densities ϱ_{0} and ϱ'_{0} diffuses, the ratio of the quantities of the two gases which diffuse per unit of time against the current is equal to:

$$\frac{i}{i'} = \frac{\varrho_{0}}{\varrho'_{0}} e^{-vl\left(\frac{1}{\delta} - \frac{1}{\delta'}\right)}$$

This quantity represents, therefore, the degree of unmixing reached in such a diffusion process; inversely the product vl is determined by the diffusion constants of the gases that are to be separated, and by the degree of unmixing required. In order to make the efficiency also as large as possible, v should be chosen as large as possible and in accordance with this l small, as follows from the equation of the current density.

The second case, which in practice has been realized, is the following one: let again v be the constant velocity of the flowing gas, and let the direction of the current be that of the negative x-axis. At a certain point in this current we now admit the other gas. This gas will then be carried along with the current, and at the same time be scattered to all sides by diffusion. In this case the distribution of the diffusing gas is found by integration of the differential equation:

$$\triangle \varrho = -\frac{v}{\delta} \frac{\partial \varrho}{\partial x}$$

with the limiting condition that at infinity the density of the diffusing gas must be zero. When the point where the gas enters the current, is chosen as origin of the system of coordinates, and the radius vector is called r, we find the solution:

$$\varrho = \frac{C}{r} e^{-\frac{v}{\delta} \frac{r+x}{2}}$$

in which C is a constant. The factor $\dfrac{C}{r}$ represents diffusion in the medium at rest, the exponential function which is due to the current, is of the same nature as in the first case; only instead of x. we have here $\dfrac{r+x}{2}$. If, therefore, a gas mixture is introduced into the current, unmixing takes place in this case as well. Further

the same remarks are valid here as in the first case; thus it is also practical here to choose the current velocity great and geometrical dimensions small to render the quantity attained as great as possible.

All these considerations have completely been confirmed by experiment. In order to effect the separation of gas mixtures by diffusion in a flowing gas in practice, it is first of all required that as a medium a gas be chosen that can be easily separated from the diffusing gases. This can be attained in a simple way by using a vapour as medium gas, which can be condensed after having passed the place where the diffusion is brought about. All the experiments made so far, were carried out with water vapour of 15 to 60 cm. pressure. The use of mercury vapour of lower pressure may, possibly, be still more efficient; this will be further investigated.

Fig. 1.

The chief point in the construction of apparatus for carrying out the process described above, is the production of a constant vapour current. When a gas passes over a sufficient distance through a cylindrical tube, a current is obtained with parallel stream lines, but the velocity is not constant; it decreases from the axis towards the walls of the tube, as is represented in fig. 1. It is, however, possible to get a current of constant velocity, though over a short distance only, when the gas passes through a wide tube with a suddenly decreasing diameter or when the gas escapes from a vessel through a small hole in the wall. When in this way the medium gas flows from a vessel A into a vessel B (fig. 2), and when the gas mixture that is to be separated, is admitted to the vessel B, the case of diffusion against the gas current is realized. The velocity of the current can then always be chosen such that only the

Fig. 2.

component of the gas mixture that diffuses more rapidly, diffuses against the current and reaches the vessel A, from which it can be pumped off together with part of the medium gas.
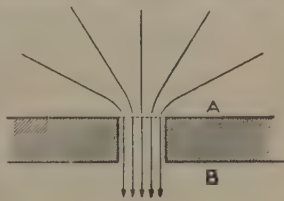
This idea was carried out experimentally as follows: the water vapour generated in a vessel heated electrically, flows through S (fig. 3) into a tube closed at the bottom by a metal plate D of a thickness of 1 m.m. This circular plate of a diameter of 28 m.m. has 30 holes of 1 m.m., each, distributed uniformly over its surface. Through these holes the water vapour enters the vessel V, the lower part of which is surrounded by a cooling jacket, so that

the water vapour is condensed. The gas mixture to be separated is admitted through the tube G. A part of this mixture diffuses against the current through the holes in D; this part can be pumped off with part of the water vapour through the tube H. The temperature of the water in the cooling jacket must be regulated in such a way, that the sum of the partial pressure of the water vapour and the pressure of the gas mixture in the vessel V is exactly so much smaller than the pressure of the water vapour admitted through the tube, that the required current velocity is obtained. The appliances used to attain this regulation, will be discussed later. The method described has so far been chiefly used to separate helium-neon mixtures, and has proved very satisfactory. Even, when the process of diffusion was executed only once, from such a mixture containing $30\,^{o}/_{o}$ helium, helium could be obtained, the purity of which was so great, that in a Geissler-tube at a pressure of 1 m.m. the neon-lines were not visible with an ordinary spectroscope. Considering the exceedingly great spectral sensitiveness of Helium with regard to very small quantities of Neon, this shows already a very great degree of purity.
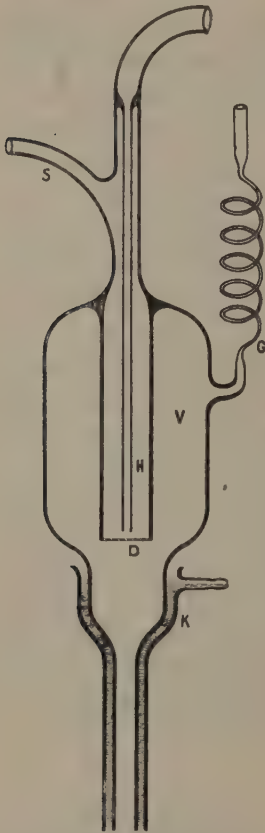
Though the unmixing of the gas mixture by diffusion against the gas current was

Fig. 3.

actually as great as was to be expected according to theory, the quantities obtained remained below expectation. This may be explained by considering, that in the method described only part of the cross section of the vapour current is used, because the gas must diffuse from the outside into the jets that issue separately from each hole. In order to deal with greater quantities another apparatus appeared to be more suitable, working according to the second example discussed above. This second case is in so far much more easily realized, as it is not necessary here to keep the current velocity accurately constant. It is immediately seen that with a current as represented in fig. 1, also unmixing of a mixture is to be expected, when this mixture is introduced at a point in the axis of symmetry of the current. The principal part of the

apparatus is reproduced in fig. 4. The water vapour enters through the tube R, which is ground off at the end, so that the water vapour leaves the tube in a cyl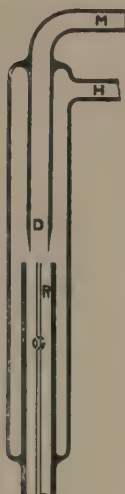indrical jet. The gas mixture enters through the tube G, ending in a capillary concentric with R, the end of which is in a plane with the endplane of R. Opposite the tube R at a distance of 3 mm. there is a tube D, the opening of which is formed by a circular sharp edge of a diameter of 6 mm., and manufactured from metal for the purpose. The outer part of the cylindrical jet coming from R is as it were peeled off by the sharp edge. With a suitable choice of the current velocity this outer part of the vapour current practically contains only the component of the mixture which diffuses more rapidly ; this component is separated from the water vapour by condensation, and collected in a vessel. By far the greater part of the gas mixture admitted through G passes on through the tube M with the inner part of the vapour current, is also freed of the water vapour by condensation, and again admitted through G by means of a circulation pump.

Fig. 4.

If the apparatus is to work well it is chiefly necessary that the velocity of the current is accurately regulated, and besides it is practical to lead the condensed water vapour back ; else the water in the heating vessel would diminish too rapidly. Fig. 5 represents the whole apparatus. In the glass vessel W, which is 50 cm. long and has a diameter of 10 cm. the water is heated electrically by means of a heating wire wound on a layer of asbestos. The pressure of the water vapour in this space can be determined by means of a thermometer T suspended in the vapour. This water-vapour flows through a tube to a bulb B, and from there to the tube R of the diffusion apparatus, while simultaneously the gas mixture to be separated, enters the tube G through a very narrow capillary tube. By the regulation of the pressure of the gas mixture before it enters the capillary tube, an accurate control of the velocity with which the mixture is admitted, is made possible. The two parts, into which the gas current is split up by D, pass on through the tubes $H\,M$ resp. and reach the condensation vessels C_1 and C_2, which are provided with cooling jackets K_1 and K_2. Here the water vapour is condensed, and the water runs back, to W as is seen in the figure. The part separated by diffusion is collected in C_1, and the rest of the gas mixtures in C_2. Both

these parts tog ether with some water-vapour leave the appara-
tus each through a very narrow capillary. The water vapour is removed by freezing it out. The separated part is received in a vessel, the rest of the gas mixture, however, is again led back to the apparatus by means of a circulation pump.
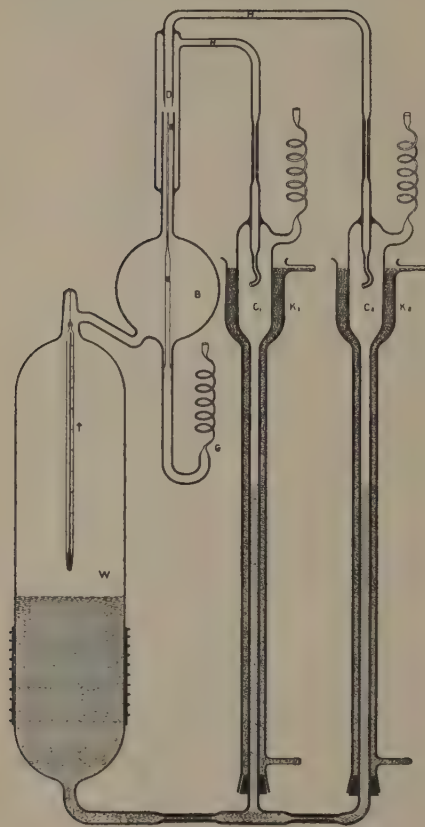
The vapour current is controled by regulating the current in the heating spiral wound on W, and the temperatures in K_1 and K_2. The latter is effected in such a way that the water flowing through the cooling jackets with accurately constant velocity is beforehand led through a copper tube, surrounded by a heating coil, so that the temperature of the water depends on the current passing through this heating coil. The check on the current velocity is made possible by the capillaries between H and C_1, and between M and C_2, these causing a difference of pressure between W and C_1 resp. C_2 that is in direct

Fig. 5.

ratio to the current velocity in H resp. M. This difference of pressure can be measured by the difference of level between the condensed water in C_1 resp. C_2 and the water in W. Neither the absolute value of the current velocity nor the temperature of the water in K_1 and K_2 need be known; when the level of the water in the two tubes with regard to the level in W is such, that the unmixing of the gas mixture is satisfactory, the heating current need only be regulated so, that this position is maintained.

It is not necessary to keep the temperature, and with it the density of the vapour, accurately constant, for both the current velocity corresponding to a given difference of pressure between the ends of the capillary tube, and the diffusion constants of the diffusing gases are approximately inversely proportional to the density of the

vapour; accordingly the relation $\dfrac{v}{\delta}$ characteristic of the diffusion in a flowing gas is not affected by small fluctuations in the vapour density. In order to prevent condensation of the water vapour against the walls, the whole apparatus is enclosed in a box, in which the air is heated a few degrees above the temperature in W.

The same degree of the separation is obtained by the first and the second method. As regards the quantity obtained the second method however, is considerably better. Only when it is required to separate small quantities, the former method is preferable, as in the second method a certain minimum quantity is required for the circulation.

It is of importance to consider whether our method of the diffusion in a gas current is more efficient with regard to the separation of isotopes than the methods used up to now. This new method is no doubt superior to the usual way of separation by diffusion. It is, however, possible, that when we apply this method to gases with diffusion-constants differing as little as they do for isotopes, small irregularities in the current may have much greater disturbing influence than in neon-helium mixtures. Nor can it, of course, be expected that a mixture of isotopes should be completely separated by a single process of diffusion, for such a process, supposing it be possible in principle, would require a very long time, as can be calculated from the above given formulae. On the other hand, e.g. in neon, a change in the ratio of mixing of the isotopes of about 30 °/ₒ could be expected as the result of one process of diffusion, so that it might be expected that a fairly far advanced separation can be obtained after not too many repetitions. It is not our intention to use the apparatus described above for the separation of isotopes, as it must undoubtedly be possible to construct apparatus on the same principle, working considerably more rapidly.

Eindhoven, 1922.　　　　　*Physical Laboratory of the*
"N.V. Philips' Gloeilampenfabrieken."
(Philips' Incandescent Lamp Works).

Physics. — *"On the Excitation and Ionization Potentials of Neon and Argon"*. (Appendix). By Dr. G. HERTZ. (Communicated by Prof. P. EHRENFEST).

In the measurements of the excitation and ionization potentials of neon and argon discussed recently [1]), the value of 20,45 Volts measured by FRANCK and KNIPPING was used as the first excitation potential of helium, in order to determine the absolute value of these potentials. Since then LYMAN [2]) succeeded in measuring the spectrum of Helium in the extreme ultra-violet directly. It can be shown from his results, that the values found by FRANCK and KNIPPING for the critical potentials of helium, like HORTON and DAVIES' values, which are in close agreement with them, are too high. As FRANCK [3]) shows by a comparison of the values measured optically and electrically, 19.75 Volts must now be taken to be the first excitation potential, which value is accurate within 0.1 Volt. In connection herewith the excitation and ionization potentials of neon and argon, having been measured relatively to helium must also be diminished by 0.7 Volt so that the following values are obtained:

Neon: Excitation potentials: 16.65 and 18.45 Volts.

Ionization potential : 21.5 Volts.

Argon: Excitation potentials: 11.55; 13.0 and 14.0 Volts.

Ionization potential : 15.3 Volts.

The conclusions relating to the optical spectrum are not affected by this correction, as only the potential differences are used for them. Only the term 0.5 s., which corresponds to the normal state of the atom, must be diminished, and becomes 174000 ± 1000 for neon, and 124000 ± 1000 for argon.

Eindhoven.   *Physical Laboratory of the · N.V. Philips' Gloeilampenfabrieken.*

[1]) These Proc. Vol. XXV N⁰. 5 and 6, p. 179.

[2]) TH. LYMAN, Nature, 110, 278, 1922.

[3]) J. FRANCK, Zeitschrift f. Phys. **11**. 155, 1922.

Physics. — *"Further experiments with liquid helium. Q. On the electric resistance of pure metals etc. X. Measurements concerning the electric resistance of thallium in the temperature field of liquid helium."* (Comm. N°. 160a from the Physical Laboratory at Leiden). By Prof. H. KAMERLINGH ONNES and W. TUYN.

§ 1. *Object of the research. Method of preparing the resistances.* The place of thallium in the periodic system of elements, between the super-conducting metals mercury and lead, made it seem probable that it would become super-conducting at helium temperatures.

We had at our disposal only rods of thallium from KAHLBAUM[1]). From this Mr. P. J. v. D. BAAN, instrumentmaker of the Phys. Lab., extruded wires of 0.2 and 0.5 m.m. thickness; they were bright at first, but quickly became tarnished and grey in colour. At the distance of a few c.m. from the ends of each wire a second short wire was melted on in a small gas-flame; during this process the thallium was protected from oxidation by a layer of melted candle grease. The wire was then wound bifilarly upon a porcelain tube with a double screw thread baked into it, (these tubes were made by the Königliche Porzellan-Manufaktur, Berlin and have been mentioned before in Comm. N°. 152c § 2) and then the four thallium ends were each soldered to a copper wire, previously attached to the tube. The resistance thus prepared was enclosed in a glass tube made by the chief glass blower of the Phys. Lab. Mr. O. KESSELRING, in the following manner. The ends of this tube through which the copper wires protuded were platinised, coppered, provided with copper caps and sealed up (see also Comm. N°. 133d, p. 60). To remove the oxidation layer on the *Tl*-wire the resistance was rinsed through the opening at the other end of the glass tube and dried by a moisture absorber and carbon tube; a tap attached

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[1]) According to a letter from the firm the thallium contained the usual amount of lead; about other impurities nothing was said. The same letter said that the firm did not prepare any "extra" pure material. M. LEVIN (Z.S. f. An. Chem. 45 (1905). p. 31) states that KAHLBAUM-thallium contains 99,91% Tl, N. KURNAKOW, S. ŽEMCZUŽNY and V. TARARIN (Z S. f. An. Chem. 83 (1913), p. 200), only say that they used pure Tl from KAHLBAUM.

to this end of the tube was then closed. By means of a Töpler pump and a suitable arrangement of glass connecting pieces the resistance was then twice rinsed with helium and finally helium to a pressure of 51 c.m. was admitted; after this the glass tube was sealed at the narrow part provided for the purpose. (For the final form see fig. 2 of Comm. N°. 160b.) In this way in Dec. 1916 were prepared Tl-VIII-1916, diameter 0.2 m.m. with a joint in the bifilar wire, and Tl-IX-1916, diameter 0.5 m.m.

§ 2. Zero determinations. For determining the zeros, the resistances Tl-VIII-1916 and Tl-IX-1916 were placed in glass tubes filled with liquid paraffin (owing to the war conditions no isopentane could be had) or with distilled benzine; the tubes were closed by corks, over which a layer of paraffin was laid. They were placed in ground ice, and the first measurement was made two hours later and repeated with intervals of about half-an-hour. The method of measuring used is either that of overlapping shunts in accordance with KOHLRAUSCH, or that of the compensation of the potential at the terminals of an unknown and a known resistance, connected in series, by means of a compensation apparatus free of thermo-forces in accordance with DIESSELHORST and provided by O. WOLFF. Enclosing the wires

TABLE I.

Datum.	Tl —VIII—1916.	Tl.—IX—1916.
5 January 1917.		1.149_0 Ω
6 January 1917.	4.439 Ω	
	Immersed in liquid air.	
8 January 1917.	4.441_5 Ω	
	Immersed in O_2 liq. and H_2 liq.	
30 January 1917.		1.150_7 Ω
2 February 1917.	4.447_5 Ω	
6 February 1917.	4.448 Ω	1.150_5 Ω
13 February 1919.	4.446 Ω	
19 February 1919.	4.446 Ω	
20 February 1919.		1.150_2 Ω

in an atmosphere of helium proved to be completely sufficient; the results of the zero point determinations are found in Table I (see p. 444). The zero point measurements are partly due to Dr. J. M. BURGERS, now Professor at Delft.

§ 3. *Measurements in liquid helium; determination of the vanishing point temperature.* The resistances were placed in the cryostat provided with a stirring apparatus shown in Comm. N°. 124c, fig. 4. For determining the amount of their resistance the second method mentioned in § 2 was used. The measurements were always made with both directions of current in the circuit of the resistances, care being taken that to each of them the direction of the current in the compensation apparatus corresponded. More-over, in measurements below the vanishing point temperature the galvanometer was observed when the current was reversed in the circuit of the resistances only (this betrays super-conductivity more quickly): in the case of super-conductivity there must be no change of position observable.

The temperatures are determined by the measurements of the vapour pressure of the helium bath, the connection between pressure and temperature having been derived graphically from the results in Comms. N°. 119 and N°. 147b. Close to the vanishing point temperature the pressure of the bath was followed with the katheto-meter (June 5th 1919); we give below the diagram of a series of observations (in this field of temperature 1 m.m. pressure = about 0.01 of a degree).
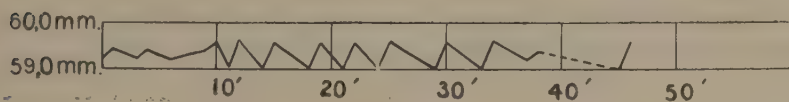

Fig. 1.

In spite of the fact that the wires were not in contact with the liquid helium, in the measurement of their resistances the galvano-meter reacted with surprising rapidity to the changes of tempe-rature of the bath. The results are given in Table II.

From Table II it appears that a constant difference Δw exists for all temperatures; in spite of this additive resistance [1] of Tl-VIII-*1916* with regard to Tl-IX-*1916* both become super-conducting at the same

[1] If this additive resistance is taken constant, it becomes $0,00083\,W_0 = 0,0037\,\Omega$; we must assume in the meantime that it is largely due to the joint.

temperature. The behaviour of Tl-VIII confirms the experience gained with Pb-wires (Comm. N°. 133d § 15), that joints in a wire do not affect its becoming super-conducting. The unsteadiness of the resistance at 2°.33 K. is caused by the pressure variations of the bath over a range of 0.6 m.m. Hg, corresponding to 0.006 of a degree;

TABLE II.

p_{Helium} in local m.m. Hg.	T.	$W_{Tl\text{-}VIII\text{-}1916}$	$W_{Tl\text{-}IX\text{-}1916}$	$w_{Tl\text{-}VIII} = \left(\dfrac{W}{W_0}\right)_{Tl\text{-}VIII}$	$w_{Tl\text{-}IX} = \left(\dfrac{W}{W_0}\right)_{Tl\text{-}IX}$	$\Delta w = w_{Tl\text{-}VIII} - w_{Tl\text{-}IX}$
	273°.09 K.	4.446 Ω	1.150$_2$ Ω	1.00000	1.00000	
	4.24	0.0075	0.0009$_6$	0.0016$_8$	0.0008$_4$	0.0008$_4$
	3.33	0.0069	0.0008$_3$	0.0015$_5$	0.0007$_2$	8$_3$
80.-‖	2.49	0.0067	0.0007$_9$	0.0015$_1$	0.0006$_9$	8$_2$
70.-‖	2.42	0.0067		0.0015$_1$		
65.-‖	2.38	0.0066$_5$	0.0007$_8$	0.0015$_0$	0.0006$_8$	8$_2$
60.-‖	2.34	0.0066	0.0007$_6$	0.0014$_9$	0.0006$_6$	8$_3$
59.3	2.33	swings from 0.006$_6$ to 0.002	swings about 0.0007	swings from 0.0014$_9$ to 0.0004$_5$	swings about 0.0006	
58.6	2.33	0.00000	0.00000	0.00000	0.00000	

in this field of temperature thallium is in the same condition as is shown for mercury in Comm. N°. 133*a* p. 24, fig. 6. At a current
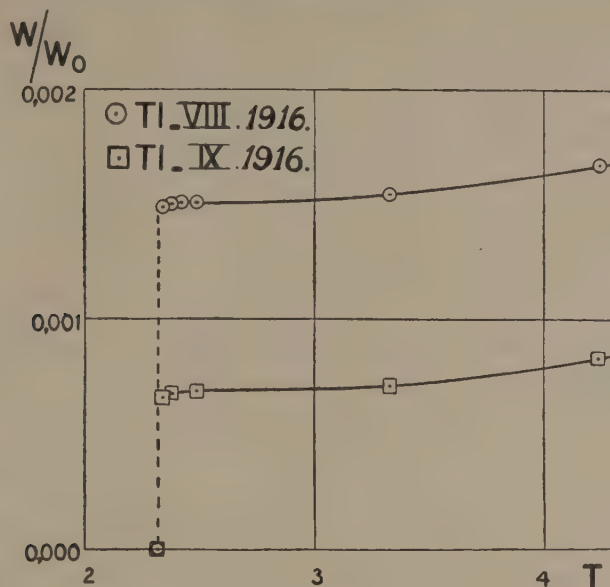

Fig. 2.

strength of 3,1 m.A. through the resistances the resistance falls, thus, within a smaller temperature range than in mercury; a similar difference had been found earlier between mercury and tin.[1] *At* $T = 2°.32$ *K. all measurable resistance has disappeared.*

§ 4. *Highest limit of a microresidual resistance.* This limit is found from the quotient of the smallest observable potential difference and the threshold value of the current, it being assumed that OHM's law still holds. We found:

15 April 1919, for *Tl*-VIII $\dfrac{W}{W_{273°.K.}} < 14.10^{-10}$ at $p = 2.3$ m.m. Hg and

27 May 1919, for *Tl*-IX $\dfrac{W}{W_{273°.K.}} < 24.10^{-10}$ at $p = 2.6$ m.m. Hg.

The difference in the results may be due to the inequality of temperature, but more to the difference of current threshold value of the two wires (see further § 5). If the value $\dfrac{W}{W_{273°·K.}}$ for thallium

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[1] This comparison is defective, for as yet the fall of resistance in mercury, tin and thallium not has observed on wires of the *same* diameter by using the *same* strength of measuring current. [Note added in the translation.]

is compared with that for other super-conductors (Comm. N°. 133d, p. 67) the retrogression of the limit caused by a greater decrease of temperature below the vanishing point temperature would seem to be recognisable in the measurements of wires of different metals, as has been ascertained already by measurements of one wire of one metal. But we must point out that this general conclusion cannot be drawn before the value of the threshold current as a function of $T_{\text{vanishing point}} - T$ and of the dimensions of the wire is known and after it has been ascertained whether a returning resistance is due to a single "bad place", or whether it is distributed over the whole length of the wire.

§ 5. *Threshold value.* At some temperatures we tried to determine the treshold value of the current, that is the strength of the current sent through the wire, which again generates a measurable potential difference. The results are given in Table III.

The two first observations in Table III show that for wires of different diameter at the same temperature the quantity $\dfrac{i}{r}$ seems to be much more a constant than the current density. The latter quantity occurs in the expression for the magnetic field at the surface of the wire through which a current passes.

F. B. SILSBEE [1]) drew special attention to the influence of this field. The determination of the threshold value of the magnetic field for thallium by means of external fields, and the comparison of it with H, derived from the two first observations in Table III by means of $H = \dfrac{2i}{r}$, (the wires Tl-VIII and Tl-IX therefore being regarded as straight), must prove whether these two strengths of field are equal, and that therefore the magnetic field is the primary factor in the disturbance of super-conductivity. Then the "bad places" referred to more than once, are the places with the smallest diameter; the returning of the resistance caused by the current, occurs first in these places only. The above mentioned experiment with thallium is prepared and also a similar one on a more extensive scale with the more easily manipulated tin; it must not be forgotten, that at the return of the resistance at great strengths of current such a development of heat soon takes place, that first the wire and if this melts the galvanometer is in danger; this makes the determination of large current threshold values rather risky.

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[1]) F. B. SILSBEE, Scient. Pap. Bur. of Stand. No. 307 (1917).

TABLE III.[2]

Date.	Resistance.	Diameter in m.m.	Section in m.m.^{2}	p_{He} in m.m. local Hg.	Temperature[1]	Threshold value in amp.	Current density in Amp. per m.m.^{2}	$\frac{i}{r}$ in $\frac{Amp.}{m.m.}$
25 April 1919	Tl-VIII-1916	0.2	0.031	2.3	1.3_6 K.	1.5_7	50.0	15.7
27 May 1919	Tl-IX-1916	0.5	0.196	2.6	1.3_8	3.6_0	18.4	14.4
»	»	»	»	55 à 56	2.29	0.25_3	1.3	1.0
5 June 1919	»	»	»	54	2.28	0.62_5	3.2	2.5
»	»	»	»	58	2.31	0.12_6	0.6	0.5

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[1] The two first temperatures in this table are derived graphically by means of a formula slightly differing from that given in Comm. No. 159 in the „Discussion".

[2] Referring to § 3 concerning the heat conductivity of helium vapour, yet the threshold values might have been found greater, when the resistances would have been surrounded *directly* by liquid helium. [Note added in the translation].

If we assume, that in super-conductivity the current runs only in an extremely thin layer at or along the surface of the wire and that each element of a section of this layer ceases to be super-conducting at a certain current saturation dependent upon the temperature, integration over the whole layer yields the threshold current and for wires of different diameter we get the constancy of $\frac{1}{r}$.

The assumption of current saturation along the surface does not, however, explain the connection, suggested by SILSBEE, between the threshold values of the current and the magnetic field.

Physics. — *"Further experiments with liquid helium. R. On the electric resistance of pure metals etc. XI. Measurements concerning the electric resistance of ordinary lead and of uranium lead below* 14° *K."* (Comm. N°. 160*b* from the Physical Laboratory at Leiden). By Prof. H. KAMERLINGH ONNES and W. TUYN.

§ 1. *Object of the research. Method of preparing the resistances.* In Comm. N°. 133*d* § 13,3 we reported that "Kahlbaum" lead became superconducting at the boiling point of liquid helium, and remained so at 4,°3 K., the highest temperature attainable with the usual cryostat for liquid helium; in § 15 of the same Comm. from the threshold value of the current at 4,°25 K. the vanishing point temperature was estimated at about 6° K. The object of the investigation described below was to establish the vanishing point temperature of lead more accurately, as well as to trace the difference in the vanishing point temperature of lead and uranium lead (*Ra G*) and to follow the course of the change in the resistance of lead with the temperature above the vanishing point, if possible up to 14°,0 K, the lowest liquid hydrogen temperature. Regarding a possible difference of vanishing point temperature for isotopes it seemed not impossible that the occurrence of the superconductivity might be influenced by the mass of the nucleus. [1]).

For the preparation of the resistances we used "Kahlbaum" lead and uranium lead (*Ra G*), of which Prof. HÖNIGSCHMID of Vienna very kindly put 16,5 gr. at our disposal; the atomic weight of ordinary lead from non-radio-active sources is 207,20, that of *Ra G* from BRÖGGERIT used is 206,06 [2]). Wires were drawn from both kinds of lead and resistances prepared from them in the manner described in § 1 of Comm. N°. 160*a*; the chemical properties of the metal

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[1]) Concerning the properties of isotopes see the article by K. FAJANS in the Elster-Geitel-Festschrift (Vieweg) and the Presidential Address to the American Association at Baltimore, Dec. 1918 by T. W. RICHARDS.

[2]) According to a letter from the firm of May 17th, 1916, "Kahlbaum" lead contains a trace of Cu and Fe, the total impurity is less than 0,01%; in a letter of Dec. 8th, 1916 they give a more precise calculation of impurity: 0,002% Cu and Fe. For an account of the atomic weight of lead isotopes cf. F. W. ASTON "Isotopes", London 1922.

made it possible to extend less care on them than on the preparation of the Tl-resistances, so that it is not necessary that the resistances should be shut off from the air in a glass tube with helium gas. We used the resistances Pb-1919-B, diameter 0,5 m.m. not enclosed in a helium atmosphere, Pb-1919-I, diameter 0,12 m.m.

enclosed in a helium atmosphere and *Isotope* Pb-1919-I, in dimensions as much as possible the same as Pb-1919-I and treated in the same way.
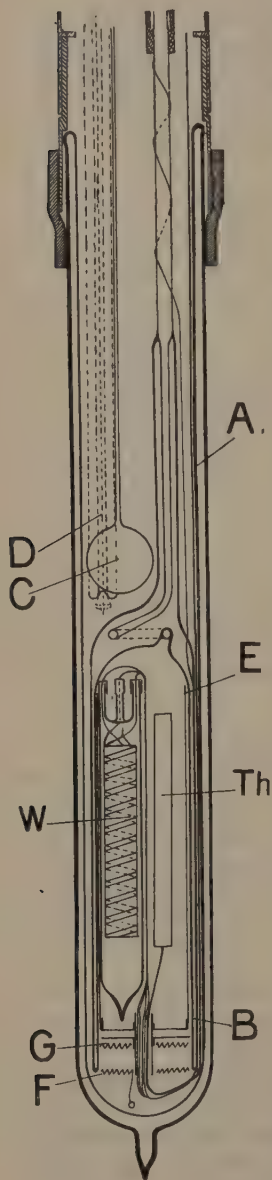
§ 2. *Arrangement of the cryostat.* The cryostat with which the experiments were made, is executed by and under the supervision of the chief of the Techn. Dep. of the Cryog. Lab., Mr. G. J. Flim. Roughly speaking, it is the same as that described in Comm. N°. 124b. A characteristic of the present cryostat is that objects to be measured are surrounded by helium vapour or gas (the latter at very low temperature); by using it, the temperature field between the boiling point of helium (4°,2 K.) and the lowest temp. obtainable with liquid hydrogen (14°,0 K.) is bridged over for the first time. For the arrangement see fig. 1. In the entirely silvered vacuum glass A, an also entirely silvered vacuum glass B hangs in an inverted position, ending in a single silvered glass tube; the bell-shaped space inside this glass is the experimental chamber. In this space are found the resistances (in fig. 1 there is only one, marked W) and the heliumgas-thermometer Th. The upper end of B opens out outside the cryostat and is connected with the gasholder; B is there provided with a regulating tap K for blowing off (not visible in the drawing). The liquid helium comes in through the entrance D; the floater C shows the height of the helium level. If the tap K, leading to the gasholder, stands open, the helium will fill both A and B; at the beginning of the experiment measurements can thus be made at the boiling point of liquid helium. If the

Fig. 1.

tap K is closed, the helium vapour formed will quickly drive the liquid helium out of the bell-shaped cryostat space; by opening the tap K and putting on the electric heating in the spiral F, a constant vapour stream may be sent through the cryostat; the stream may be brought to the temperature desired by electric heating of the spiral G; thus the liquid level of the evaporating helium remains between F and G. The copper mantle E inside the bell contributes to the acquiring of an even temperature over the whole space; further experiments must show in how far uniformity of temperature has been achieved with the arrangement as described. The first cooling uses a great deal of liquid helium.

§ 3. *Resistance and temperature determinations.*

The resistances are measured by comparison of the deflections of the galvanometer, when connected with the extremities of an unknown and a known resistance (0,001 or 0,01 Ω O. WOLFF); the resistances are proportional to the means of the deflections for both directions of the current, as follows from the comparison of the deflections for 0,001 and 0,01 Ω.

The temperatures are determined with a heliumgasthermometer of constant volume and with open manometer, the height of the barometer is read from an aneroid. In the measurements of May 18th 1920 the zero pressure of the thermometer was calculated to be about 1140 c.m.; as it was not easy to determine this pressure accurately, the pressure at the temperature of liquid helium was taken as calibration point (this temperature followed from the vapour pressure of the bath).

For the measurements of May 28th 1920 the zero-pressure of the thermometer was decreased to 290 cm., in order to have less difficulty with the corrections on the provisional international Kelvin scale, these corrections in and below the field of liquid hydrogen being insufficiently known. As two calibration points the tensions of the thermometer served, placed in liquid helium (May 28th 1920) and in liquid hydrogen (May 29th 1920); the temperatures of these points again follow from the vapour pressure of the bath, using the data from Comm. N°. 147b and N°. 156b.

For the correction of the indications of the thermometer on the provisional international Kelvin scale, we had at our disposal the data of Comm. Suppl. N°. 34a, p. 17, note 4 (obtained from the data of Comm. N°. 102c), in which $B_{-254° C.}$ has been taken zero,

TABLE I.

Temp.	B.		Δt [1] (Pressure heliumthermometer at 0°. C. = 1000 m.m.).	
	Old observations.	New observations.	Old observations.	New observations.
20°.5 K.	0.00000	− 0.00010		+ 0.04$_5$
19.1	− 0.00305		+ 0.03$_9$	
4.29			+ 0.05$_1$	+ 0.05$_2$
4.22		− 0.00347		
3 71		− 0.00420		+ 0.05$_3$
3.44		− 0.00538		+ 0.05$_7$

Further we have made use of the newly calculated Δt's, and from this we deduce table II.

TABLE II.

	Filling I. $p_{0°C}$ = 1140 c.m. May 18, 1920.				Filling II. $p_{0°C}$ = 290 c.m. May 28 and 29, 1920.			
$T_{\text{vapour tension}}$	Δt	$T_{\text{He, uncorrected}}$	p in local m.m. Hg.	$\dfrac{p}{T_{\text{He}}}$	$T_{\text{vapour tension}}$	Δt	$T_{\text{He, uncorrected}}$	p in local m.m. Hg.	$\dfrac{p}{T_{\text{He}}}$
4°.20 K.	0.60	3.60	151.8	42.1$_6$	20.37 K.	0.13	20.24	209.7	10.3$_6$
					4.22 K.	0.15	4.07	42.7	10.4$_8$

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[1]) $\Delta t = (T-T_0)\left(\dfrac{T_{100}\,B_{100}-T_0\,B_0}{100\,v}\right) - \left(\dfrac{T B_T - T_0 B_0}{v}\right)$, in which v is the volume of gas in the thermometer, expressed in the theoretic normal volume; the C's may, according to calculation, be neglected even with a large density.

and also from Comm. N°. 119 § 5b $B_{4°,29K.} = -0.000047$ [1]); Table
V of Comm. N°. 156a gives a resumé of the corrections, calculated
with the above data. In accordance with note 1 and 3, p. 27,
Comm. N°. 156a here $B_s = 0,000499$, $B_{100} = 0,000476$, $\alpha_{iHe} = 0,0036614$ are taken, and the influence of the C's is neglected [2]).

New determinations, to be published shortly, of helium isotherms
at $T = 20°,5$, $4°,2$, $3°,7$ and $3°,4$ K. gave provisional new values
for B, which therefore infer the introduction of different corrections
in the provisional intern. Kelvin-scale; they are larger than those in
Table V, Comm. N°. 156a and they do not come into line so well
with those for higher temperatures. For the sake of completeness
we give a comparison of these in Table 1. (cf. p. 387).

§ 4. *Temperature of the vanishing point.* On May 18th and 28th
1920 all three resistances proved superconducting in liquid helium
and behaved, therefore, in the usual way. After this the cryostat
was gradually brought to a higher temperature by electric heating
of the vaporised helium. At a certain moment the galvanometer
moved quickly over 35 c.m. on the scale and the vanishing point
was apparently reached; the suddenness of the deflection speaks
well for the usefulness of the cryostat if not too high demands are
put upon it. A repetition of the heating (very gradually) confirmed
the first result. While the temperature was kept constant the thermo-
meter was read at the vanishing point. The results are given in Table III.

TABLE III.

Data.	Filling.	$p_{\text{gas thermom. in local m.m. Hg.}}$	$T_{\text{He, uncorrected}}$	$\angle t.$	$T.$
May 18, 1920.	I	263.6	6.2_5	0.58	6.8 K.
May 28, 1920.	II	73.9	$a.\ 7.0_8$	0.15	$a.\ 7.2_3$
			$b.\ 7.1_3$	0.15	$b.\ 7.2_8$

[1]) The $B = -0,000047$ is that derived according to $pv = RT + \dfrac{B}{v}$; the B's
further mentioned in this number are those according to $pv = RT\left(1 + \dfrac{B}{v}\right)$, in
agreement with the change of notation mentioned in note 360 of Comm. Suppl. N°. 23.

[2]) These values for B_0, B_{100} and $\varkappa_{iHe}$ must be retained to get the corrections
on the provisional internat. Kelvin-scale. Measurements have shown that it would
have been more correct to use $B_0 = 0,000513$, $B_{100} = 0,000492$ and $\varkappa_{iHe} = 0,0036613$ (Comm. N°. 102b, Table I and Com. N°. 156a, p. 22, note 1); this
would lead to a *second* provisional intern. Kelvin-scale (helium-Avogadro-scale) for
which reason we retain the first B's.

In filling II a is calculated by interpolation between calibration points 20°,24 and 4°,07 K., b by using only the calibration point 20°,24 K. in the same way as in filling I only calibration point 3°,60 K. needed to be used.

The agreement between the measurements with filling I and II is bad. If in filling II we calculate, with the pressure increase of 10,3⁶ mm. per degree, the temperature of the helium on May 28th, 1920, the calculation yields 4°,27 K, while the vapour pressure gave 4°,22 K (table II); this is in favour of the measurements on May 28th. If we further take the large Δt's in filling I into consideration, a determination with filling I deserves less confidence than one with filling II. *We take T vanishing point lead $= 7°,2 K$,* although it is still desirable to make a more accurate determination.

§ 5. *Comparison of the vanishing point temperatures of lead and uranium lead (Ra G).*

On May 18th, 1920 the cross-thread of the kathetometer was adjusted to the mercury meniscus in the open tube of the thermo-meter at the pressure belonging to the vanishing point temperature of *Pb*-1919-*I* (the meniscus in the closed tube must of course always be kept on the same mark).

After a decrease of temperature *Isotope Pb*-1919-*I* was inserted in the resistance circuit and the temperature again raised. If the galvanometer moved, because the resistance passed through the vanishing point, the meniscus in the tube of the thermometer passed the cross thread; this phenomenon was certain up to 1 mm. Hg: *"Kahlbaum" lead, atomic weight 207,20 and uranium lead (Ra G), atomic weight 206,06 have the same vanishing point temperature within the accuracy of $^1/_{40}$ degree.* The same result was yielded by *Pb*-1919-*B*; an influence of the smaller current density in consequence of the larger diameter could not be detected (the strength of the measuring current was always 7,8 m.A.).

§ 6. *Resistances above the temperature of the vanishing point.*

The results of these measurements are given in fig. 2; the point most to the right, placed within a square, is the result of a mea-surement in liquid hydrogen. As vanishing point 7°,2 K was taken. To make the curve join on properly to the one in the field of liquid hydrogen it must be traced as in the diagram; that is why corres-pondence with the points marked is defective. The broken crosses have the following meaning: if the difference between the vanishing

point temperatures found on May 18th and May 28th may be attributed entirely to Δt having been taken too large on May 18th, all the other temperatures must be recalculated, this recalculation yields the crosses. Although this approximation is theoretically not quite correct, as $T - \Delta t$ and not T ought to rise at every temperature in the same ratio, yet the results are in favour of the suggested assumption.
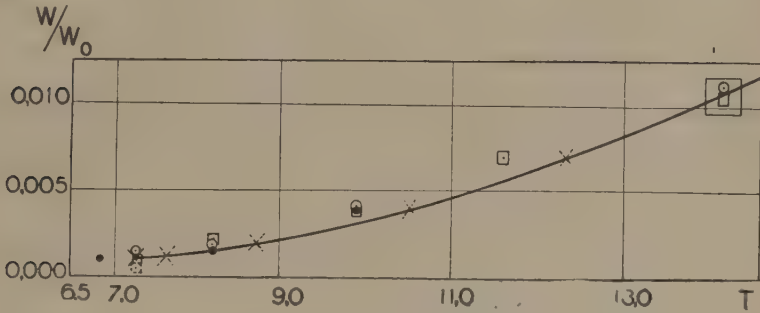

Fig. 2.

● $Pb-1919-I$,
⊙   *Isotope Pb—1919—I*,   } 18 May 1920.
⊞ $Pb-1919-B$,
⌷ $Pb-1919-B$,   28 May 1920.
✕ Reduced observations : § 6.

Chemistry. — *"The Action of Sodiumamide on Pyridine, and some Properties of α-aminopyridine"*. By J. P. WIBAUT and ELISABETH DINGEMANSE. (Communicated by Prof. A. F. HOLLEMAN).

Through TSCHITSCHIBABIN'S [1]) beautiful researches α-aminopyridine has become easily accessible. This investigator found that sodium amide acts on pyridine as follows:

$$C_5H_5N + NaNH_2 = C_5H_4N.NHNa + H_2.$$
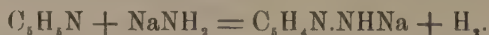
On decomposition of the reaction product with water, aminopyridine and sodium hydroxide is formed.

As we required this substance as starting material for synthetic investigations, we have applied the method of preparation found by TSCHITSCHIBABIN. Though also in our experiments α-aminopyridine was formed as chief product, we found other substances than the Russian investigator among the by-products.

We experienced that the action of sodium amide on pyridine can take place in different ways, dependent on the nature of the sodium amide preparation used. We have prepared sodium amide according to TITHERLEY'S indication by the action of carefully dried ammonia on melted sodium at 350—400° C. The preparation obtained was a pure white, showed a crystalline fracture, and contained no free sodium. This preparation did not react with pyridine. A preparation prepared at 300°, reacted very slowly with pyridine. In this experiment very little α-amino pyridine was however, formed; further a little γ-γ-dipyridyl, and some other products, which we did not examine.

A sodium amide preparation of KAHLBAUM, which was pretty impure, as it contained free sodium and also sodium hydroxide, acted vigorously on pyridine, as TSCHITSCHIBABIN states. Another preparation of KAHLBAUM, which was apparently much purer, acted in exactly the same way. A mol. of pyridine is diluted with toluene, and this mixture is heated with a mol. of finely powdered sodium amide at 120—125° for seven hours.

[1]) Journal de la Société Physico-Chimique Russe, **46**, 1216 (1914).
Chem. Zentral Blatt 1915. I. 1065.

We have decomposed the reaction product with water according to Tschitschibabin's direction, dissolved it in ether, and distilled it at a pressure of 15 m.m. The bulk went over at 104—125°, and was almost pure aminopyridine in agreement with the records of the investigator mentioned. At 130—180° and 15 m.m. an oil distilled, which soon gets a dark colour when exposed to the air. After some time white crystals separated out of this oil. Recrystallized out of water these crystals became colourless, long needles melting at 73°. This substance is the hydrate of γ-γ-dipyridyl, which has already been described by Anderson. After drying in a vacuum exsiccator we obtained the γ-γ-pyridyl itself, which melts at 112°. We identified this substance by analysis and by oxidation with potassium permanganate. We obtained white crystals melting at 307°, which agrees with the melting-point of iso-nicotinic acid. On action of picric acid on γ-γ-dipyridyl, both dissolved in alcohol, we obtained a picrate crystallizing in fine yellow needles, and melting at 252°. As appears from analysis this picrate contains 1 mol. of picric acid to 1 mol. of γ-γ-dipyridyl. With anhydrous acetic acid and zinc dust the γ-γ-dipyridyl gave the intensive violet colour reaction, which was lately described by Dimroth and Heene.

There are still some more substances to be found in the oil that distilling at 130—180° and 15 m.m. pressure. After the bulk of the γ-γ-dipyridyl had been removed from this oil, we treated the liquid with hydrochloric acid. Two chlorides were then obtained, which both crystallized in white needles. After recrystallisation from diluted hydrochloric acid one melted at 115—116°; the second melted above 280°. The latter substance appeared to be the salt of γ-γ-dipyridyl.

We have liberated the base from the chloride of 115—116°, and obtained white crystals melting at 94—95°. This melting-point agrees with the α-α-dipyridyl-amine $(C_5H_4N.)_2NH$, which was obtained by Steinhäuser and Diepolder [1]) from α-chloro pyridine and α-amino pyridine by heating with barium oxide.

The nitrogen percentage of our crystals, which melt at 94—95°, agrees with the value calculated for dipyridyl amine.

Tschitschibabin says that this dipyridyl amine is formed through the action of two molecules of pyridine on 1 mol. of sodium amide, but does not yet describe the experiments from which this appears. When speaking of the action of 1 mol. of pyridine on 1 mol of sodium amide (the same way as we performed the reaction) Tschit-

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[1]) Journ. f. prakt. Chem. **93**, 393 (1916).

Schibabin does not mention the dipyridyl amine. He prepared the dipyridylamine from α-chloorpyridine and α-aminopyridine by heating with zinc chloride, and gives as meltingpoint 86—87°.

We have prepared a picrate from the dipyridylamine, which melts at 227°.

Our observations on the melting-points of dipyridylamine itself, on the salt with hydrochloric acid, and on the picrate of this base are in perfect harmony with Steinhäuser and Diepolder's records, so that we have no reason to doubt the identity of our preparation.

The investigation of the components of the oil that goes over at 130—180° and 15 m.m. pressure, was not yet completed then, for a large part of this oil remained liquid after treatment with hydrochloric acid. We removed the hydrochloric acid from this liquid part, and then distilled the oil at ordinary pressure. We collected three fractions, viz. of 293—295°, of 295—300° and above 300°. The first two fractions had a nitrogen percentage of 13.9 °/$_o$; the fraction above 300° had 16.4 °/$_o$ of nitrogen. From this last fraction a little dipyridylamine was still deposited. The first two fractions were joined; this liquid appeared to be strongly unsaturated: it immediately decolours a solution of permanganate and soda at ordinary temperature. We have subjected part of this liquid to the oxidation with sodium permanganate in sulphuric acid solution. A white substance, which crystallized in white leaves and melted at 74°, could be isolated. The nitrogen percentage of it was 8.0 °/$_o$. This shows that it cannot be a dipyridylamine or a dipyridyl.

Besides these crystals, a viscid liquid was obtained from the oxidation product. The investigation of these substances is being continued.

It appears from all this that on action of sodium amide on pyridine there are formed, besides aminopyridine, several other pyridine derivates, among which the γ-γ-dipyridyl seems to preponderate quantitatively. Tschitschibabin likewise observed by-products in the reactionproduct which arises from sodium amide and pyridine. After the α-aminopyridine had been distilled off, he states that an oil went over which distilled at 120—180° and at 15—20 m.m., and besides a fraction that went over at 180—250° and 15—20 m.m.

From the fraction of 120—180° crystals are deposited which, after recrystallisation from benzene, melted at 158°. Tschitschibabin supposed these crystals to be γ-aminopyridine, but he could not identify the substance for want of material. From the oil distilled at 180—250° this investigator isolated the α-α' diaminopyridine; there were also other substances present, which he did not identify.

In many experiments we prepared some hundreds of grammes of amino pyridine; the reaction always proceeded as we described above. We never observed a substance with a melting-point of 158°; nor did we ever observe a diamino pyridine.

Accordingly the action of sodium amide on pyridine can evidently give rise to the formation of different substances. We have not been able to find out why with some sodium amide preparations amino pyridine was not formed. Addition of small quantities of water or free sodium had no influence on this. We also caused sodium to act on a mixture of pyridine and toluene, both at the ordinary temperature and at the temperature of boiling. In this case there was formed a tough amorphous mass, insoluble in water and in organic solvents, soluble in acids. By extraction with ether we could isolate only a small quantity of γ-γ-dipyridyl. This result is in accordance with the early experiments of ANDERSON.

The formation of the important quantities of γ-γ-dipyridyl in our amidisation seems, therefore, not to be in connection with a possible percentage of sodium in the sodium amide preparation used.

As amino pyridine seems comparable with aniline, we examined the action of oxidizers on this pyridine base. For so far as we know, nothing is known about this.

Bichromate and diluted sulphuric acid change a diluted solution of amino pyridine only slowly at ordinary temperature. When the mixture is left standing for some days, the liquid gets dark. From this solution an amorphous green substance is isolated, insoluble in water, alcohol, and ether, soluble with emerald green colour in diluted hydrochloric acid. On evaporation of the hydrochloric acid an amorphous blue substance was left behind. At 90° the action of sulphuric acid and bichromate on amino pyridine takes place more violently; and amorphous products are also formed. In these experiments part of the amino pyridine however remained unchanged.

The action of potassium bichromate in acid solution on this base takes place much less rapidly than in case of aniline.

The action of potassium permanganate proceeds in an entirely different way. Amino pyridine is rapidly changed by permanganate in acid solution; after a few minutes all the permanganate has disappeared. When a diluted solution of amino pyridine is added to a diluted permanganate solution containing soda, a slow action takes place. When, however, first a neutral permanganate solution is added to a diluted solution of amino pyridine, and then a few drops of 10% sodium hydroxide, a change of colour is immediately seen. When we start from a 0.1% solution of amino pyridine, the

liquid first becomes dark violet, then pure blue, after a few minutes the colour has become emerald green. This green colour does not change again, when there is no excess of permanganate present. If the solution of the amino pyridine is somewhat more concentrated, the green colour at once sets in after a transient dark colouring.

This reaction is characteristic of amino pyridine and very sensitive. In acetyl amino pyridine this colour reaction does not set in at the ordinary temperature until after some hours, soon however on boiling.

Whether the acetyl rest is split off primarily here, has not yet been examined.

A more detailed account of the observations discussed briefly here will be published in the Recueil des Travaux chimiques.

Physics. — *"On Centres of Luminescence and Variations of the Gas Pressure in Spectrum Tubes at Electrical Discharges"* II. [1] By Dr. L. HAMBURGER. (Communicated by Prof. H. A. LORENTZ).

§ 1. *Introduction.*

Experiments made by the author in **1916** showed that continuous current-discharges when passing through not too rarefied gases, gave rise to differences of pressure, the value of which, with sufficient current density can amount to thirty per cent of the total pressure. A first communication on this subject appeared in the author's thesis for the doctorate in the beginning of July 1917 [2]. In these investigations such variations of pressure were observed in numbers of gases of very different natures, as argon, neon, helium, nitrogen, hydrogen; it was found that the effects observed are very great in argon, hardly perceptible in hydrogen, and it was seen that the pressure effect must increase with the intensity of the current (loc. cit. p. 94), and with ·the root of the moleculair weight (loc. cit. p. 107).

Four months after the publication of this Thesis for the Doctorate F. SKAUPY [3] published a short paper, in which he mentioned differences of pressure in continuous current discharges observed by him (only) in the case of noble gases; these differences of pressure were small compared with the effect found by us owing to the small current density applied by him.

In April 1920 the author of this communication [1] published some further theoretical views and quantitative calculations about the effects found, F. SKAUPY confining himself in the course of the same year to some qualitative remarks [4], which indeed referred more to the phenomenon of electro-striction, which in our opinion can only play a subordinate part.

Finally in the middle of 1922 there appeared a publication by A. RÜTTENAUER [5] on an important experimental investigation, in

[1] Cf. for I: L HAMBURGER, These Proc. Vol. XXIII N⁰. 2 and 3, p. 379.

[2] L. HAMBURGER, Thesis for the doctorate, Delft 1917. Cf. These Proc. **20**, 1043 (1917). Zeitschr. f. Wissensch. Phot., **18**, 1 ('19).

[3] F. SKAUPY, Verh. d. Deutsch. Phys. Ges. **19**, 264 – '67. Nov. Heft, '17.

[4] F. SKAUPY, Zeitschr. f. Physik **2**, 215. Aug. Heft, '20.

[5] A. RÜTTENAUER, Zeitschr. f. Physik **10**, 269—274 ('22).

which the variations of pressure of noble gases were subjected to a closer examination and the dependence of the effects found on different variables was given in an approximative "empirical" formula.

§ 2. *Purpose.*

After having thus established our priority, we set ourselves the task:

1st. to show that the experimental results obtained by A. RÜT-TENAUER in his extension of the investigations on the pressure effect correspond to the theoretical formulae developed by us in I, in which also the practical part of RÜTTENAUER's empirical formula is included;

2nd. to prove that serious objections may be raised against SKAUPY's theoretical view of the pressure effect;

3rd. to draw further conclusions from RÜTTENAUER's important determinations, also in connection with our earlier data on this subject, and our objective, quantitative determinations on light emission in continuous current discharges in spectrum tubes likewise published in our Thesis.

§ 3. *Formula for the calculation of the pressure-effect.*

RÜTTENAUER gives the empirical formula:

$$\triangle p = f \frac{Ag \sqrt{M}}{p} \cdot \frac{l}{Q}$$

in which $\triangle p$ represents the difference of pressure found, f a constant, A the current density, g the gradient of tension, M the molecular weight, p the total gas pressure, l the length of the pos. pile, Q its cross section.

It is seen from this that RÜTTENAUER finds experimentally that the pressure effect would be in inverse ratio to the total gas pressure [1]), whereas the author of this paper found — also experimentally — that with not too great variations of p, $\triangle p$ varied little, if at all, with p. [2])

How is this difference in result to be accounted for?

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[1]) Which was, indeed, also mentioned by F. SKAUPY in his first publication (1917).

[2]) RÜTTENAUER is erroneously of opinion that it would have been found both by me and by SKAUPY that in argon the pressure effect is in inverse ratio to the gas pressure. It was on the contrary observed by us that within certain limits the pressure effect showed a very slight variability with regard to the gas pressure.

On comparison of Rüttenauer's researches with ours it appears that we made use of comparatively narrow capillary tubes as circuit of the current, the German investigator on the other hand of comparatively wide tubes. We derived, however, already before, that two different formulae must be valid for these cases, and this as a consequence of the fact that in the case of wide tubes the laws of Poiseuille should be applied when taking the diffusion phenomena into account, for narrow tubes those of Knudsen-Langmuir. For in the first case the electric mass-transportation $c_1 \dfrac{A\,Q}{a\,p}$[1]) may be put equal to:

$$c_2 \frac{D^4}{l}(p_2 - p_1) \sqrt{\frac{T}{M}}\text{[2])*}$$

in the second case to:

$$c_2 \frac{D^3}{l}\frac{p_2 - p_1}{p} \sqrt{\frac{T}{M}}\text{[3])*}$$

In the first case the theoretical formula for the pressure effect — taking into account that $Q = \dfrac{\pi D^2}{4}$ for tubes with round cross-section — is equal to:

$$p_2 - p_1 = \Delta p = f_1 \frac{AQ}{ap}\frac{l}{D^4}\sqrt{M} = f_1 \frac{A}{a'p}\cdot\frac{l}{Q}\sqrt{M}\ .\ \ \ . \quad (I)$$

in the second case to:

$$\Delta p = f_2 \frac{AQ}{a}\cdot\frac{l}{D^3}\sqrt{M} = f_2 \frac{A}{a''}\cdot\frac{l}{D}\sqrt{M}\ .\ \ \ . \quad (II)$$

in which

$$f_1 = \frac{c_1}{c_2\sqrt{T}}\ ,\quad f_2 = \frac{c_1}{c_2\sqrt{T}},\quad a' = a\cdot\left(\frac{4}{\pi}\right)^2\ \text{ and }\ a'' = a\frac{4}{\pi}$$

When on grounds to be given later, the gradient g is taken inversely proportional to a, we may write equations I and II as follows:

$$\Delta p = f\frac{Ag}{p}\cdot\frac{l}{Q}\sqrt{M}\ \ .\ \ .\ \ .\ \ .\ \ . \quad (III)$$

resp.

[1]) In which c_1 is a constant. Compare further Equation 9, p. 390, These Proc. XXIII, No. 2 and 3. The factor Q has been introduced, because A now denotes current *density*. in our former paper current *intensity*.

[2]) Compare Equation 3, p. 382, These Proc. XXIII, No. 2 and 3, 1920.

[3]) Compare Equation 1, p. 382, loc. cit.

*) These equations have been obtained from the Equations 1 and 3, p. 382, These Proc. XXIII, 2 and 3, after multiplication by 1 p. This has been done on the strength of what was said in footnote 3, p. 385 of our paper of 1920.

$$\Delta p = f \, Ag \, \frac{l}{D} \, V \overline{M} \quad . \quad . \quad . \quad . \quad . \quad . \quad (IV)$$

in which equation *III* must be valid for tubes the diameter of which is large with respect to the free path of the corpuscles, which is actually the case in RÜTTENAUER's experiments. It is seen that equation *III* is identical with RÜTTENAUER's empirical approximative formula.

§ 4. *On the influence of the potential gradient on the pressure effect.* The "empirical" introduction of the potential gradient by RÜTTEN-AUER in the pressure effect equation rests on the testing by three kinds of observations:

a. the dependence of the observed values of the pressure effect on the potential gradient with one and the same current tube and the same gas with different current densities.

b. the dependence when the diameter of the discharging tube is varied;

c. the dependence when the nature of the gas is changed.

With reference to, *a* we must remark that a critical consideration of the values published by RÜTTENAUER shows that the variation of the gradient is irregular, and besides smaller than the deviation of the values found for $\dfrac{p \, \Delta p}{Ag.l V \, M}$ interse, which values should be approximately constant. Thus in table 4 p. 272 of RÜTTENAUER's publication the gradient for argon varies e.g. between 1,87 and 2,36, while the "constant value" $\dfrac{p \, \Delta p}{Ag.l V \, M}$ as a maximum varies between 3,70 and 4,98. For the rest the uncertainty in the determinations of the gradient seems to have been considerable. Where in our Thesis the gradient decreased with increase of current density, it appears to increase in a slight degree in the investigations recorded by RÜTTEN-AUER in table 3, whereas it decreased in a great degree in table 5. For this category of cases a constant value had, therefore, better be substituted for *g*, and the empirical formula becomes identical with our theoretical equation *(I)*.

This is, therefore, in harmony with the statement expressed in our former publication (loc. cit. p. 390) that "in the case that the nature of the bearers is not modified" (hence for a definite gas) and "with not greatly varying tension" (potential gradient) *a* is a constant.

With reference to case *b* we remark that the experimentally determined influence of *g* is unmistakable. So far as the consequences of

g for a definite gas are concerned, this influence is also theoretically comprehensible. It already follows directly from the equation (4) of our former communication (I loc. cit. p. 384) which is based on the equation of motion of the electrically charged particles in the electric field, and from which appears the proportionality with the potential gradient V, provided the nature of the bearers undergo no change with V.

Already for this reason we may express this also in the equation of the mass-transportation by the electric current:

$$\text{mass-transportation} = \frac{1}{a} \; Q \cdot A \cdot \frac{760}{p} \cdot 2{,}32 \; 10^{-4} \; {}^{1})$$

(equation (9) communication I), by replacing $\frac{1}{a}$ there by a factor bg, in which b is a constant for a definite gas. Hence $\frac{1}{a.g} = b$ or $ag = \text{constant}$.

Let us also try to derive this directly from the nature of the electric conduction, and at the same time ascertain from it whether or no b has the same value for different gases. We then remind the reader that equation (9) of communication I teaches us that the pressure effect must be proportional to the part $\frac{1}{a}$ of the conduction, which takes place through ions charged with mass. This part is in direct ratio to the concentration of the ponderable ions. The problem may, therefore, be reduced to the question whether increase of g can cause increase of the concentration of the ions. In case of proportionality the equation $ag = constant$ may then be applied. *)

This relation will actually have validity for electropositive and noble gases, when J. Franck and G. Hertz's [2]) elementary theory is adopted, according to which, as is known, perfectly elastic collisions between electron and atoms are assumed to take place, till — under influence of the electric field — the electron has passed over such a distance, and in this has obtained so much energy that its energy exceeds the value connected with the ionisation tension. The greater g, the shorter the time in which this value is obtained; the

[1]) With regard to the factor Q in the numerator, see note 1, p. 465.

*) We neglect the electrons liberated at the formation of the positive ions, supposing that within stationary conditions as many of these electrons are disappearing by recombination and formation of negative ions charged with mass. Additionally it may be remarked, that in the field of this investigation the number of ions compared with the number of free electrons is very small.

We intend to deal within short time more fully with this part of the subject.

[2]) J. Franck and G. Hertz. Verh. d. D. phys. Ges. **18**, 213 ('16).

number of ionisations per time-unit will be directly proportional to g.

Later FRANCK and HERTZ [1]), just as C. D. CHILD [2]), in connection with N. BOHR's theory have assumed that unelastic collision can also already take place before the tension of ionisation has been reached, in which then removal of one of the electrons of the atom to a path lying more outward, takes place. On return to the normal path this energy can then be emitted. Yet the result of the elementary theory will be approximated by three cases:

I. Through absorption of the radiated energy by neighbouring atoms (COMPTON) [3]).

II. By increase according in quanta of the energy of slow electrons on collision with dislocated atoms ("collisions of the second kind" in the theory of O. KLEIN and S. ROSSELAND; cf. also § 5).

III. (In a slight degree) through the renewed collision between dislocated atom and (rapid) electron, before the former has lost energy by radiation (K. J. VAN DER BIJL [4])).

In agreement with our conclusion from equation (4) communication I it may therefore really be expected that in approximation the relation $a \cdot g = const.$ will hold for each of these gases separately, so long as the nature of the bearers is not subjected to any characteristic modification. For in this case the energy-compensation ensuing from I—III will always be the same percentage. This compensation must, however, be very different for different gases. So that, the tensions of ionisation also being so greatly divergent, we are led to accept the obvious conclusion that the value of $a g$ will be different for different (noble) gases. We shall revert to this when discussing c.

That for the rest deviation is to be empirically observed $ad\ b$ between a calculation based on formula III and observation (chiefly as a consequence of errors of observation), may appear from the following example (argon); though formula III would lead us to expect that the value:

$$\frac{Q \cdot p \cdot \triangle p}{A g \sqrt{M\,l}} \cdot 10^6$$

would be constant, a consideration of the values published by RÜTTENAUER shows that in table 5 e.g. the "constant" which amounts to about $2,3 \cdot 10^{-5}$, for one and the same noble gas in a definite case (in which the pressure varies from 0,5 to 0,64 mm., the current density from 1,49 to 1,21 A/cm². and the *bore of the tube from*

[1]) J. FRANCK and G. HERTZ. Phys. Zeitschr. **20**, 133 ('19).

[2]) C. D. CHILD. Phil. Mag. (6) 278 ('14). Phys. Rev. (2) **15**, 33 ('20).

[3]) K. T. COMPTON. Phys. Review (2) **15**, 476, 1920.

[4]) K. J. VAN DER BIJL. Phys. Rev. **10**, 546 ('17).

$2,01\ cm^2.\ to\ 0,454\ cm^2.$) shows the maximum deviation of $0,7\ .\ 10^{-5}$.

In opposition to the fact of such a maximum deviation of about $30°$, it may be stated that the values of the tension gradient for one and the same gas in RÜTTENAUER's observations inter se are to each other as a maximum as 1 to 4. We therefore consider (see also our calculation for nitrogen p. 472 footnote) the effect of g exceeding the errors of observation to be present.

We consider the fact of this theoretical and empirical determination of the approximated *proportionality of the pressure effect* with Ag, hence *with the added energy*, of great importance. It is in perfect harmony with the proportionality of the light emission of the pos. pile with the added energy, which had been established by our objective measurements. We will presently come back to this point of simultaneous and quantitative parallelism. (See § 5).

With respect to case c we already remarked that divergent values should be expected for ag resp. b for different gases. This is opposed to RÜTTENAUER's view; for this investigator thinks — with reference to his empirical formule — to be allowed to consider the pressure effects comparable for different kinds of gases, and assumes f to have the same value for different gases. In our opinion the way in which RÜTTENAUER introduced g into the empirical formula of the pressure effect, cannot very well be accepted. He was in this evidently led by the results for argon and helium (table 4 of his communication); in fact we find here only a maximum deviation of about $15°/_0$ [1]). Besides on the ground of the theoretical expectation, we have, however, reason to think here of chance, also on the ground of what follows. In the absence of determinations of the value of g, neon has not been taken for a comparison by RÜTTENAUER in the corresponding calculated constants. For this purpose we can, however, derive with amply sufficient accuracy from the determinations of the terminal voltage communicated in our Thesis that under comparable circumstances the potential gradient in neon amounts to about $2\frac{1}{2}$ times that in argon [2]). When we, therefore,

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[1]) In RÜTTENAUER's tabel 4 we find for helium and argon for the same tube a maximum deviation in the "constant" $\dfrac{p\,\triangle\,p}{Ag\,\sqrt{M1}}$, which amounts to about $4,6\ .\ 10^{-5}$, of a value of $0,75\ .\ 10^{-5}$

(in which p varies from 0.618 to 0,776 m.m.)
(„ A „   „   1.36   „   1.21 amp./c.m.^{2}).

[2]) In the derivation from the terminal voltage cathode- and anode gradient have been taken into account. That irregularities at the electrodes cannot play an important part in our case, appears among other things when also the ratio of the tension-gradients for argon and helium are derived from the terminal voltages;

place the values of $\triangle p$, A, and p found for neon (Rüttenauer, table 1 of his publication) in his table 4, we can write $g = 5$ for neon, g being put at 2,0 for argon. Then we find:

TABLE A.

Tube		p	Ap	A	g	$\dfrac{p\,Ap}{Ag\sqrt{Ml}} \cdot 10^5 = $ constant
III $l = 60$	Neon	0.776	0.026	1.13	5. –	1.33
III $l = 60$	Argon	0.741	0.062	1.21	2.0	4.98
III $l = 60$	Helium	0.785	0.079	1.13	9.67	4.73

in other words the value of the "constant" is from 300 to 400°/₀ higher for argon and helium than for neon. This shows in our opinion that it is injustifiable to put the pressure effects for different gases comparable on such a basis.

Conclusion. It is necessary to replace Rüttenauer's empirical formula by the théoretical formula:

$$\triangle p = f \frac{A\sqrt{M}\,l}{D^3} \cdot \varphi(g) \quad \text{resp.} \quad \triangle p = f \frac{A\sqrt{M}\,l}{p\,D^4} \cdot \varphi(g)$$

in which $\varphi(g)$ represents a function of the tension gradient, which in definite regions can approximately assume the form bg, in which b represents a constant the value of which is not the same for different gases.

§ 5. *Region of validity.*

We pointed in our previous communication that the phenomena in the path of the current are very complicated, and that our formulae are drawn up for more or less idealized cases. What makes A. Rüttenauer's determinations also so interesting is that they were carried out with noble gases, in which the conditions in the path of the current are naturally much less complicated than in the multi-atomic not-noble gases. Besides this investigator used a very long and wide positive pile, which brings out the influence of what happens in the positive pile better.

We mentioned already that in his second publication F. Skaupy

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then the ratio appears to agree with that which ensues from the values of the potential gradient as they have been measured by A. Rüttenauer with the positive pile.

as appears from some remarks, was inclined to the belief that the pressure effect might be referred to the phenomena of electrostriction. On page 215 loc.cit. it says about this: „In meiner schon erwähnten Arbeit über die Druckdifferenzen wurde gezeigt, dass bei Argonröhren innerhalb eines gewissen Druckgebietes (etwa 0,5 bis 3 mm. Hg) die sich bei einer gegebenen Stromstärke einstellende Druckdifferenz zwischen den Enden der 600 mm. langen, 0,8 cm. weiten Röhre umgekehrt proportional dem in der Röhre herrschenden Druck war. Durch einen Irrtum wurde diese Beziehung für alle Edelgasse als gültig angenommen und darauf eine Theorie der Erscheinung gegründet. Diese kann wohl nicht richtig sein, da die Beziehung nur für Argon in dem genannten Druckgebiet erfüllt ist, aber nicht z. B. für Neon oder Helium."

We point out, however, that A. Rüttenauer does not only find the dependence on p for argon, but also for the noble gases neon and helium, so that here no argument is present to induce us to look for the central point of the explanation of the phenomena in another region. We also remarked before that already in 1880 D. Bos[1]) showed that the effects which can ensue from the electrostriction for gases, are exceedingly small.

Besides, as we could show that the region covered by A. Rüttenauer quantitatively continued that examined by us, if only the right laws of diffusion are applied for every region, the validity of our theoretical conception is confirmed for investigations in which

TABLE B.

$\triangle p/p$	as	1.3	to	50	or	ca.	1 to 40	
Q		0.03	to	2	or	ca.	1 to 70	
p		0.15	to	1.2	or	ca.	1 to 8	
A		0 66	to	12.7	or	ca.	1 to 20	
g		0.6	to	45	or	ca.	1 to 75	2)
M		4	to	40	or	ca.	1 to 10	
l		5	to	60	or	ca.	1 to 12	

[1]) Diss. Groningen.

[2]) That for the tension gradient in this record of the ratios also observations made on nitrogen, are included, may be justified thus. We published the following measurements already before: $p_1 = 1.18$ m.m. Hg. Terminal voltage 288 V. $l_1 = 6.5$ c.m. $q_1 = 3.15$ m.m.^{3}. $M_1 = 28$, $A_1 = 12.7$ Amp. c.m.^{3}, $p_1 = 0.18$ m.m. $p_2 = 0.15$, $l_2 = 5$, $q_2 = 3.15$, $M_2 = 28$, $A_2 = 12 7$. For nitrogen in uviol-glass with $Q = 3.15$ m.m.^{2} there are known to the author (Tabel C) the following three observations of p in connection with the terminal voltage, from which we arrive at the bracketed values for the potential difference between the ends of the positive pile

the values of the different quantities, are as a maximum to each other in the ratio as recorded in table B.

Continued experimental investigation on others than the examined gases but also on the latter themselves can, however, still reveal much. For all these investigations have been made within limits for which it may be assumed that the nature of the luminescent centres and of the current-conducting ions does not undergo any essential change. We pointed out before that it follows from the researches of J. STARK [1]), A. WEHNELT and J. FRANCK [2]) that when p is sufficiently reduced, and y sufficiently raised, the pressure-effect reverses it sign [3]). It may, however, also be questioned, what happens, when the nature of the discharge is maintained, but the current-density is greatly increased. We know only one indication of an essential change taking place in this case; already in I we expressed [4]) the desirability of examining by means of continued investigations of the pressure-effect, whether anything could be derived from this

[by making by estimation, an approximate calculation of the cathode and anode gradient and the loss of potential between the electrodes end the entrances of

TABLE C.

p in m.m. Hg	Terminal voltage	Pot. diff. pos. column	Thesis
0.34	212 Volt	(ca. 170 Volt)	table 4
1.19	288 „	(ca. 240 „)	„ 10
2.38	350 „	(ca. 290 „)	„ 14

the capillary path of the current]. Extrapolating we then find for $p = 0.15$: pot. gradient in the pos. pile: about 145 Volts. If in connection with this we assume the pot. gradient to be $^3/_5$ at 0.15 m.m. of that at $p_1 = 1.19$ m.m.

$\left[\text{hence } \dfrac{g_1}{g_2} = \dfrac{5}{3} \right]$, and if we bear in mind that we must apply here the formula

$\Delta p = f A g \dfrac{l}{D} \sqrt{M}$, the following formula would follow from this

$$\frac{\Delta p_1}{\Delta p_2} = \frac{g_1}{g_2} \cdot \frac{l_1}{l_2} = \frac{5}{3} \cdot \frac{6,5}{5} = 2,2.$$

the ratio measured on nitrogen being $\dfrac{0,18}{0,08} = 2,3$.

More and more sharply defined measurements are very desirable also here.

[1]) J. STARK. BOLTZMANN-Festschrift 1904.

[2]) A. WEHNELT and J. FRANCK. Verh. d. D. phys. Ges. **12**, 444 (1910).

[3]) For convenience sake we shall distinguish this as "negative" effect from the "positive" effect found by us.

[4]) Communication I loc. cit. 1178.

about change of the luminescent cenires on the transition from the blue to the red *argon*-spectrum. On this head A. RÜTTENAUER's experiments give no decisive result, because the current-densities applied by this investigator, are too small. The author expresses the hope that — experimenting in this region being impossible to him for the present — this remark may induce others to undertake a further investigation.

§ 6. *Quantitative and Simultaneous Parallelism of Light Emission and Pressure Effect.*

We derived in our former publication that the pressure-effects are chiefly due to the transportation of ions by the electric current (mass-transportation), *which ions have originated at the impact between electrons and atoms.* Where the extension of the experiments corroborates our theoretical conception quantitatively, we think that it is not devoid of interest to remark here that the theory of quanta manifests its simultaneous and quantitative validity with respect to light emission and pressure effect by means of the positive pile.

We have, indeed, to do here with two typical regions of the application of the theory of quanta:

1. With light emission, the region of spectroscopy, in which the phenomena should be studied, which present themselves on the *return* of electrons from abnormal to less abnormal paths;

2. With the region of the pressure effects, in which the collisions should be studied between electrons and atoms, the formation of ions, hence*) the passing of the atom-electrons *from* normal to abnormal paths.

As soon as the "bearers" change their character, both the character of the light emission and of the pressure effect changes. The latter may reverse its sign; as regards the light emission the change finds among others a pregnant expression in the law of displacement already cited in our previous paper.

If on the other hand the electric conditions do not change characteristically, if the bearers continue to preserve the same character, our quantitative objective measurements of the light emission and our and RÜTTENAUER's manometric determinations of the pressure effect prove the *simultaneous quantitative proportionality of light- and pressure effect with the added energy.* That the light emission does not change its character through increase of the added *quantity* of energy, was only what was to be expected according to the theory of quanta. Accordingly we consider particularly the fact that the same thing holds simultaneously for the pressure-effect, a contribution

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*) As far as the positive ions are concerned.

to our knowledge. We see in this a confirmation of the view that the *atoms both absorb and emit energy in quanta*, at the same time an *interaction* between the two regions, which latter finds expression in a related region of investigation, among others in KLEIN and ROSSELAND's theory [1]).

The well-known theoretical parallelism between these two regions and the simultaneous parallelism between the observations on the pressure effects and the light emission which have now been experimentally shown *objectively*, corroborate anew the close relation, the *unity between these two classes of phenomena*.

§ 7. *Summary*.

1. Our priority with regard to the "positive" pressure effect is established.

It is shown that A. RÜTTENAUER's experimental investigations quantitatively confirm the theoretical view and formulae about the pressure effect found by us, which we gave before. This establishes confirms for an extensive region of validity defined in § 5 that the *pressure differences chiefly occur in consequence of mass-transportation by the electric current.*

2. It is desirable to replace the emperical formula given by A. RÜTTENAUER for the pressure effect by two formulae derivable from the theory, dependent on the ratio between the free path of the corpuscles and the (round) diameter of the tube, viz.:

$$\triangle p = f \frac{A \sqrt{M} l}{D^3} \cdot \varphi(g) \quad \text{resp.} \quad \triangle p = f \frac{A \sqrt{M} l}{p D^4} \cdot \varphi(g)$$

in which $\varphi(g)$ represents a function of the potential gradient, which can assume approximately the form $b g$ in definite regions; in which b represents a constant the value of which is *different* for different gases.

3. It is shown that the opinion advanced by F. SKAUPY that the pressure effect would be determined by the elastic electron impact, is untenable.

4. The significance of the simultaneous parallelism of the quantitatively and objectively measured light and pressure effects with regard to the theory of the quanta is pointed out. It confirms that the atoms both emit and absorb energy in quanta.

5. Attention is drawn to the desirability of extending the investigations, in particular also to argon.

Dordrecht, October 11, 1922.

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[1]) KLEIN en ROSSELAND. Zeitschr. f. Physik. **4**, 46 ('21).

Botany. — *"On a new clinostat after* DE BOUTER*"*. By Prof. F. A. F. C. WENT.

It has been known to every botanist for more than 15 years, that the clinostats in present use are not satisfactory with regard to great precision. Already in 1907 VAN HARREVELD[1]) made the errors of those instruments known to us in a detailed study. He himself constructed a much better clinostat, satisfying high requirements, but nevertheless introduced only in a few laboratories. This will be chiefly due to the great costs, unsurmountable for most laboratories.

To the above fact it has been chiefly due, that Mr. P. A. DE BOUTER, mechanic of the Botanical Laboratory at Utrecht, asked himself, whether it would not be possible to construct a much cheaper clinostat, nevertheless coming up to high requirements. Those considerations have led to the construction of a new clinostat, the description of which follows.

Fig. 1 shows the clinostat in a more or less schematic way. 1 is a shuntmotor, running directly full speed, and connected by a belt 3, with a flywheel 2, to the axis of which a pinion has been fixed. With the aid of cog-wheels its motion is transmitted to the proper clinostat 5. The axis of the fly-wheel turns on ball-bearings. Now the question is, to make this fly-wheel revolve exactly once a second; this cannot be attained by altering the speed of the motor or by regulating the diameter of the grooved wheels because of a too great oscillation of the voltage of the town-plant. Neither does the motor run regularly with equal voltage; namely with excentric load. For this reason a different construction has been used here.

Into the circuit $+ -$ of the motor a resistance 12 has been inserted in the form of a lamp, in consequence of which the fly-wheel runs a little too slowly, e.g. half a rotation a second. If however this resistance is put out of circuit, the fly-wheel revolves a little too fast, e.g. two rotations a second. This putting out takes

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[1]) PH. VAN HARREVELD, Die Unzulänglichkeit der heutigen Klinostaten für reiz-physiologische Untersuchungen. Recueil des Travaux botaniques néerlandais. III. 1907, p. 173.

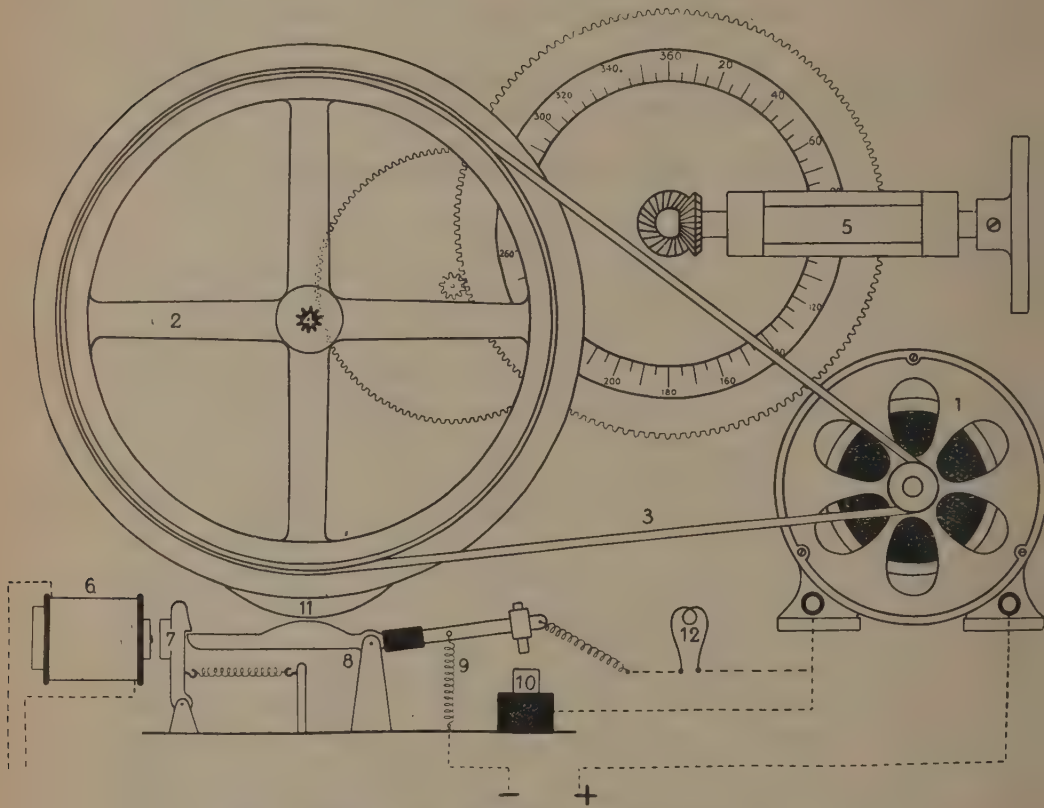place every second with the aid of the pendulum of a clock keeping
exact time.

Fig. 1. Sketch of the new clinostat; description in the text.

At 6 we see an electro-magnet every second turning magnetic
for an instant and attracting the spring-armature 7. The turning-over
switch 8 is drawn to one side by the spring 9, in consequence
of which the contact 10 is made. The current passes from + through
the motor straight to contact 10, next through a part of the switch
8, through the spring 9 and finally to —; in this way the motor
runs full speed.

But on the fly-wheel a cam 11 has been fixed; this makes the
switch 8 catch behind the armature 7, in consequence of which the
circuit is broken at 10. Then the current has to pass through the
resistance and the motor runs slower.

The final result is that the fly-wheel makes exactly one revolution
a second. Even considerable oscillations of the voltage of the light

and power-station are of no consequence, the only result will be, that the cam 11 is a little more to the right or to the left at the moment, at which the second circuit is closed, so that only the ratio of the rapidly and slowly revolving parts of the axis of the fly-wheel may be altered every second. This is of no importance, because the axis of the clinostat revolves at a much slower rate and the movement is transmitted to this by means of the cog-wheels 4, etc.

To the horizontal axis of the clinostat a conical cog-weel has been fixed, in which another conical cog-wheel catches, fastened to an adjustable axis 5. This latter axis has been fitted on in such a way, that it can revolve on the horizontal axis and can be fixed, while the rotatory movement is not impeded. This enables us to give the axis of the clinostat any desirable position. By fixing the adjustable axis and releasing the adjusting-apparatus, a rotation of the plant perpendicular to the horizontal axis may be obtained. This arrangement is shown in fig. 2; the adjustable axis is fastened with the screw A, the adjusting-apparatus with the handle B.

Fig. 3 gives a backview of the whole apparatus, in which the arrangement of fig. 2 has not yet been fitted on. This figure shows, that the apparatus is comparatively small and may easily be removed by one person. The position of the axis too may be modified without any difficulty during the experiment.

To the simple construction it is owing that the costs of purchase are considerably lower than of any other satisfactory clinostat. An objection is, that the motor keeps running throughout the experiment and therefore constantly uses current. But then the axis revolves with great power, so that considerable weights can be carried, while excentric loading that is rather considerable, does not cause any alteration in the regular running of the clinostat.

In order to check the running of this clinostat and compare it with PFEFFER's and VAN HARREVELD's clinostats, the recording-apparatus of the auxanometer of KONINGSBERGER [1]) was used.

For this purpose electrodes were fixed to the axis of the clinostat either right opposite to each other or at an angle of 90°, in such a way, that after each full rotation of the axis, the top of such an electrode once made contact in a mercurydish and in this way a circuit was closed for a short moment. Closing that circuit caused a writing glass-pen to be stopped in its course and to be

[1]) V. J. KONINGSBERGER, A method of recording growth under various external influences. Proceedings Kon. Ak. v. Wet. Amsterdam. W. en Nat. Afd. XXX, 6/7. 1921.

sent back to its starting-point, while a drum with paper, on which the recording occurred, was moved on 1.5 mm.
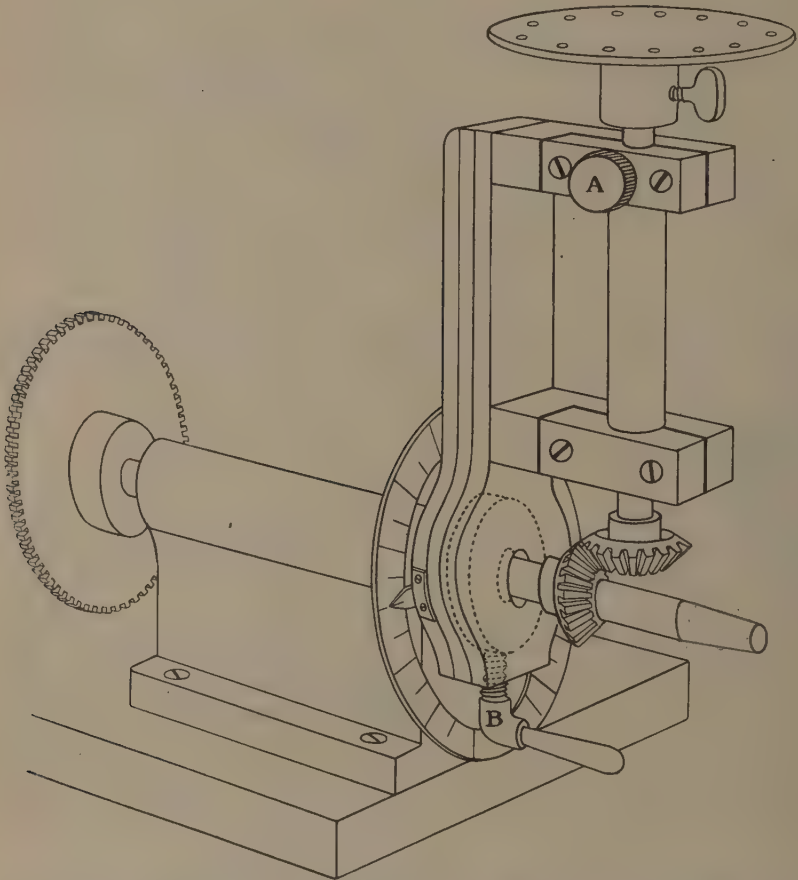

Fig. 2. Top of the clinostat-axis with conical wheels, as described in the text.

The pen moves along the paper with a velocity of 1 mm. a second, writing a straight line. A number of parallel lines arises in this way, as shown in fig. 4, drawn for so many seconds as the period amounts to, needed by the clinostat-axis to make a half or a quarter of a rotation.

If therefore the clinostat runs regularly, these lines must be of equal length, or may differ one second at most, with respect to the point of time at which the contact with the mercury is made.

In the figure something else has been recorded: every 6 minutes

a time-signal is given on a continuous line T. Of course the distance covered by the circumference of the clinostat-axis in successive 6
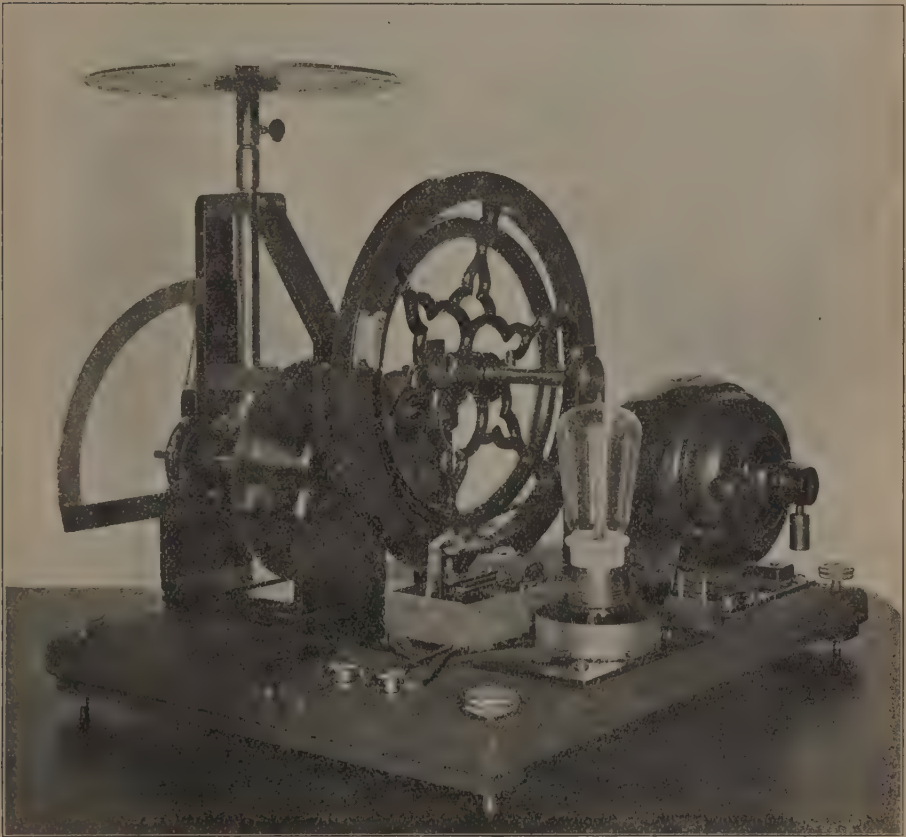
Fig. 3. Backview of the whole clinostat.

minutes must always be the same; so the distance between the time-signals must not vary with a good clinostat.

Now the various clinostats were tested in two ways; partly without load, partly with an excentric load on the axis. This latter was done, because that very unequal load causes the greatest diffi-culties in practice, especially when in the dark plants have to be fixed on a clinostat, or when we have to try several times in order to get an exact centering, when meanwhile the plants have already been exposed to the unilateral influence of gravitation for a long time. Fig. 4 shows the results of those experiments.

In I the behaviour of a clinostat of PFEFFER is shown with an excentric load, amounting to 0,26 KG. when calculated on the axis.
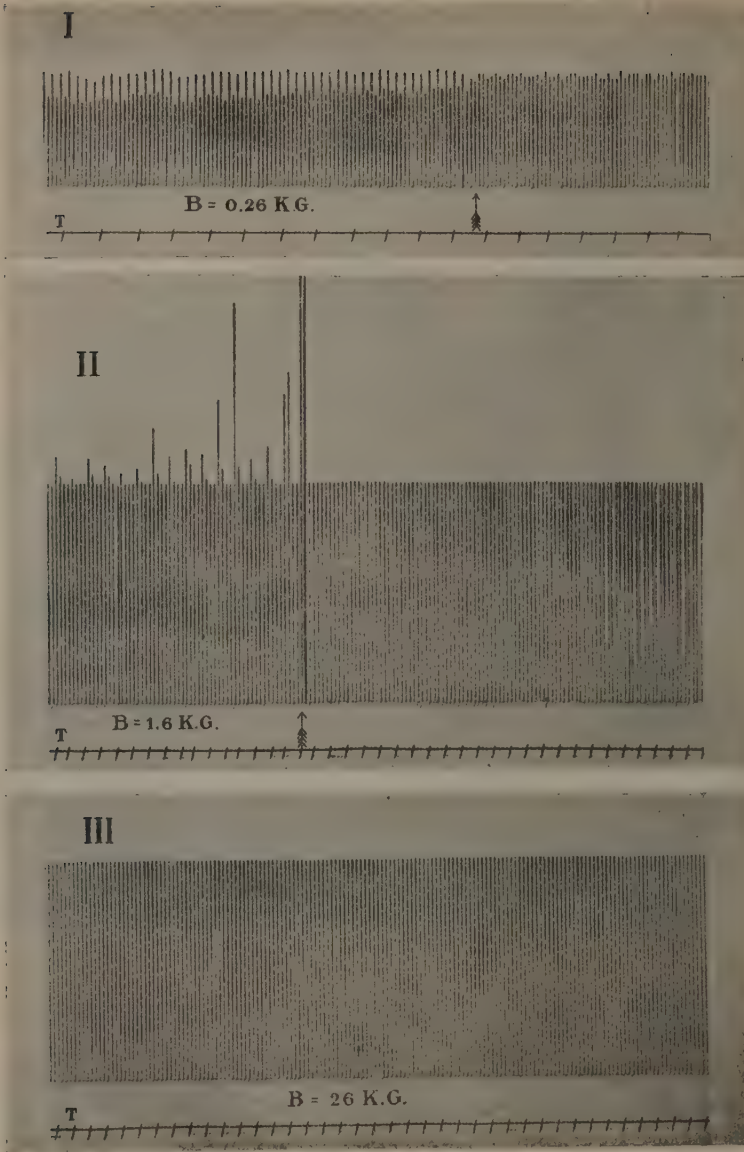
31

Fig. 4. I. Clinostat of PFEFFER. Records of half rotations.
B is the excentric overload converted on the axis. At ↑ this load
was removed. II. Clinostat of VAN HARREVELD. Record of 1/4
rotations. B as above. At ↑ this load was increased to 2 KG. at
which the clinostat stopped; next the overload was removed. III.
Clinostat of DE BOUTER. Record of half rotations. B. excentric over-
load as above. In all 3 figures T is the time-line, checked every
6 minutes.

It may be noticed how great the difference is between the two halves of the revolution, while this difference disappears beyond the arrow, indicating the moment at which the excentric load is removed.

II refers to the clinostat of van Harreveld; here the excentric load was larger, 1.6 KG., calculated on the axis and there too irregularities appear, which are sometimes very considerable. The arrow indicates the moment at which the excentric load was increased to 2 KG. The clinostat had come to a stop; this happened with a clock-weight of 13 KG. If a heavier weight had been chosen, the movement would of course have continued. After removing every excentric load, the running was perfectly regular, as appears from the rest of the figure.

III shows the working of the clinostat de Bouter with an excentric load of 26 KG. calculated on the axis. We see that notwithstanding this, it runs quite regularly, so that the superiority of this clinostat is perfectly clear from the figure.

A contemplation of the time-signals T in the three parts of the figure will necessarily lead to the same conclusion; these time-signals gave a sign after every six minutes.

Summarizing I arrive at the conclusion, that this clinostat is a great improvement on those hitherto used. Now that plant-physiology is developing more and more into an exact science, the old "a peu près" methods will have to be left and therefore care should be taken that the instruments used come up to high requirements of precision.

Utrecht, Botanical Laboratory, December 1922.

Biochemistry. — *„Concerning the Synthetic Action of Bacteria in the Paunch of the Cow"*. By Prof. B. SJOLLEMA and J. E. VAN DER ZANDE. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated at the meeting of December 30, 1922).

The question whether bacterial processes occurring in the paunch of ruminants are significant for the metabolism of these animals [1]), should be given more attention to than here to fore, since, by way of trial, ruminants are fed with urea, made from the nitrogen in the air. For the significance of the substitution of urea for protein in the animal's diet depends to a great extent on the capacity of the bacteria of the paunch to synthesize from urea, in the presence of non-nitrogenous substances, the amino-acids which the higher animals are not able to build up.

Tryptophane is one of the amino-acids indispensable to man and to the higher animals. It is highly improbable that mammals can synthesize tyrosine from non-aromatic substances.

We have tried to ascertain whether these two substances can be built up by the bacteria occurring in the cow's paunch, when, beyond ammonia no other source of nitrogen is present than urea, asparagin or aspartic acid.

Our procedure was as follows: [2])

Directly when the animal was killed, part of the contents of the paunch was brought to our Laboratory in a sterile bottle, fitted with a glass stopper [3]).

With the help of a sterile wire a little of the paunch contents (i.e. of the turbid fluid after removal of the coarser particles) was transmitted to sterile nutrient solutions, contained in Erlenmeyer-flasks plugged with cotton-cool, and which were of a depth of 1

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[1]) Here we refer to the development of volatile acids in the paunch from sugar, as demonstrated before by one of us (B. S.). See Bericht III 5th International. Congres für "angewandte Chemie" Berlin 1903, p. 825.

[2]) It was adopted because bacterial growth could not easily be recognized directly in the turbid juice of the paunch (even when much diluted), and also because we wanted quantitative data regarding tryptophane-formation.

[3]) We would here gratefully acknowledge our thanks to Mr. HOEFNAGEL and to Mr. DE GRAAF, respectively director and sub-director of the Utrecht abattoir, for their kind assistance in obtaining the material required for these experiments.

to $1^1/_2$ cm. The flasks were then left standing in an incubator at 36° C. Duplicate cultures were made for each experiment.

When the bacteria were fairly developed (which was the case after two days) one of the cultures was examined for the presence of the amino-acids, alluded to above; the other remained in the ncubator. Moreover a new culture-medium was inoculated with it. We used Uschinsky's solution, unmodified or modified as indicated below. [1])

Since the p_H of the paunch contents was about 7,4, we took care to let the p_H of our culture media be the same.

In order to demonstrate the presence of tryptophane we applied the reactions of Voisenet (with HCl, formaldehyde and nitrite) and of Hopkins-Cole (with H_2SO_4 and glyoxylic acid). Millon's reagent was used for ascertaining the presence of tyrosine. Voisenet's reagent stains differently with indole and with tryptophane. Indole after shaking out with ether was reacted on with dimethylpara amidobenzaldehyde.

Uschinski's solution, whether modified or not, but invariably without an aromatic or heterocyclic compound, inoculated with a small quantum of the paunch-contents, always gave in the sediment (obtained by centrifugation after the addition of alcohol) after a sojourn at 36° C. in an incubator, a very distinct tryptophane, and tyrosine-reaction, whereas initially the reactions were negative.

A better growth and more powerful reactions were obtained by mixing 10 c.c. of the fresh paunch fluid with 25 c.c. of Uschinski's solution.

Whereas the reactions in the sediment were invariably positive, the supernatant fluid displayed negative reactions.

In order to make sure that the tryptophane and the tyrosine reactions were not due to other indole or phenol-derivatives, the sediment was, in a few cases, centrifuged anew with diluted alcohol and once more with ether (indole). The reactions of the sediment were as distinct as before. The cultures themselves were also shaken out with ether some times. With the above-named aromatic aldehyde the ether gave a negative indole-reaction. It was evident, therefore, that neither free tryptophane, nor other free indole-derivatives, nor free phenol-like bodies were present. The positive reactions may, therefore, be attributed to the body-protein of the bacteria.

On inoculation of new Uschinsky solutions with the cultures an

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[1]) The ordinary Uschinsky-solution contains K, Na, Ca, Mg, PO₄, Cl and SO₄; besides glycerol, ammonium-lactate and sodium aspartate.

excellent growth could be noted, and after a couple of days positive tryptophane, and tyrosine-reactions of the sediment.

The present investigation, therefore, shows clearly that there are bacteria in the paunch of the cow, capable of building up trypto-phane and tyrosine with an aliphatic nitrogen-compound and with ammonia. With every one of the six paunches we succeeded in obtaining this result.

We consider the presence of tyrosine to be established when bacterial bodies show a phenol-reaction (MILLON's) The non-specificity of the tryptophane reactions is of no importance in our experiments. They are only needed to show the presence of an indole-derivative so long as tryptophane is considered as sole indole-derivative in the protein-molecule [1]).

Positive results were also obtained in the experiments in which asparagin (or sodium-aspartate) had been replaced by urea. The bacterial growth was, however, decidedly slower. The ammonium-lactate had been substituted in these experiments by potassium lactate, so that urea was the sole source of nitrogen.

After 2×24 hours the tryptophane-reactions were as a rule weak in the turbid culture solution and very clear in the sediment, which had been obtained through centrifugation.

A couple of times we added tryptophane to the USCHINSKY solution which resulted in the formation of indole contrary to the other experiments.

Direct addition of indole inhibited bacterial growth considerably; it was arrested completely by 50 mgms per 100 c.c.

Whether tryptophane can be developed from indole, as assumed by LOGIE, is not borne out by the present experiments, for, where addition of a small quantity of indole caused some bacterial growth, the formation of tryptophane may have resulted from the presence of ammonium-nitrogen or asparagine-nitrogen.

When substituting glucose for the glycerol and the lactic acid of the USCHINSKY-solution a tryptophane synthesis takes place which is almost equal to that in the ordinary USCHINSKY-solution.

In experiments under approximately anaërobic conditions the growth was inferior to that obtained in the manner above-described. An experiment, in which air was drawn through the fluid by suction, did not yield a larger growth than usual.

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[1]) Since gelatine does not yield VOISENET's, nor MILLON's reaction and proline and oxyproline are contained in it, it follows that these two amino-acids do not give these reactions.

The histidine reactions thus far obtained, were still somewhat doubtful.

Several microscopic preparations were made of the cultures. Sometimes different species were present, i.e. diplococci, rod-shaped bacteria; sometimes staphylococci and streptococci; in one case the predominance of one species was such as to render it difficult to find another. These almost pure cultures were not always made up of the same bacteria; sometimes they were small ovoid, at other times rod-shaped bacteria.

It being known that even various stocks of one and the same species may differ largely as to the chemical changes they engender, we did not ascertain whether the developing species were in any way concerned in the result of the reaction.

According to an approximate quantitative determination in a culture, three days old, the sediment of 100 cc. contained about 3 mgms of tryptophane, i.e. per Liter 30 mgms, or 3 grms per 100 L. (putting the paunch contents at 100 L.).

A man of 70 k.g. weight requires per day about $2^1/_2$—3 grms of tryptophane. Assuming the same ratio for a cow, this animal would require per day about $17^1/_2$—20 grms. The quantity necessary for the producton of milk has not been taken into account here.

Putting the tryptophane content of milk per L. at about 750 mgms, and putting the daily flow of milk at, say, 12 Liters, the animal would have to take in another quantum of 9 grms of tryptophane.

As far as we are aware tryptophane synthesis by bacteria (B. coli and B. FRIEDLÄNDER) from ammoniac and aliphatic nitrogen-compounds, has been demonstrated only once, viz. by LOGIE[1]).

From the publication of BRAUN and CAHN—BRONNER[2]), which came to our notice when our experiments had nearly come to an end, it may be inferred that their experiments also pointed to tryptophane synthesis, for they could grow coli, paratyphoid-, and FRIEDLÄNDER-bacteria when ammonia nitrogen was the only source of nitrogen present. Where they report, that under perfectly anaërobic conditions ammoniac-assimilation is impossible, even after the supply of more energy, the question rises (granting their theory to hold generally) whether in the rumination process an aërobic condition exists which allows any synthesis worth mentioning.

It may rationally be supposed that, wherever micro-organisms manage to live on inorganic or aliphatic nitrogen-sources, they them-

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[1]) J. of Pathol. and Bact. Bd. 23, 224 (1919/1920).

[2]) Biochem. Zeitschrift Bd. 131, 272 (1922).

selves derive the cyclic amino-acids from these sources, it being a fact that protein, containing these amino-acids, is always present in these organisms.

In how far the amino-acids, formed in the paunch, are of use to the metabolism of ruminants, will have to be made out by food-experiments, which will also have to show whether the bacterial protein, formed in the paunch, is resorbed.

Let it be observed that we have never succeeded in demonstrating tryptophane (or tyrosine) in the fresh turbid paunch-fluid (after the removal of the solid particles) and also that we were not more successful in this respect after cultivating for some days in the incubator, either under aërobic or anaërobic conditions.

Meanwhile we should not omit stating that reactions in a fluid like the paunch-fluid, are far less sensitive than those in unstained solutions. Only when 7 mgms of tryptophane per 100 cc. was added in the form of protein (bloodplasma) a perfectly distinct tryptophane-reaction was recognizable.

Still, the phenomenon, just alluded to, does not point to an abundant tryptophane formation in the paunch, which is the more striking since the paunch fluid with Uschinsky's solution $(10 : 25)$ yields negative results at starting, but exhibits distinct reactions after 2×24 hrs.

The above experiments show: 1°. that various bacteria present in the paunch of cows can build up the amino-acids tryptophane and tyrosine from ammonia nitrogen plus asparagine (or aspartic) nitrogen, and also from urea as nitrogen-source.

2°. that these bacteria can form quantities of tryptophane in the culture-medium of Uschinsky, which may be of some significance for the metabolism in cows; however it is not quite certain whether this synthesis is equally intense in the paunch.

(From the Chem. Labor. of the Utrecht Veterinary Univ.)